

Comparison of catalysts for hydrogen production by the ethanol steam reforming reaction.

Catalytic role of active metallic species in the ethanol steam reforming reaction pathway

[A036]

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Abstract:

A comparison among some catalysts, which have been already reported in the bibliography, for hydrogen production via the ethanol steam reforming reaction is done. The role of every studied active metallic specie (Co, Ni, Cu and Zn species) and some supports (Al₂O₃, SiO₂) in the ethanol steam reforming reaction pathway in the range of 300-500°C is found. The effect of the operation variables on conversion, yield, selectivity and catalyst stability is also studied. Taking into account that the ethanol steam reforming reaction could be a global chemical process of a small group of well known consecutive reactions, it is proposed that every different step in the ethanol steam reforming reaction can be consecutively and separately optimized using the most convenient catalyst for each one and not necessarily only one catalyst for the whole process.

Key words: Catalysts comparison; Ethanol steam-reforming; Hydrogen production; Catalytic role; Active metallic species; reaction pathway

Nomenclature:

ESRR: ethanol steam reforming reaction

WGSR: Water Gas Shift Reaction

IG: inert gases

X_i : substance i conversion

Y_i : product i yield

t: temperature in °C

$R = H_2O/EtOH$: feed relation at the reformer inlet

GHSV: Gas Hour Space Velocity (GHSV = M/F)

t_r : retention time ($t_r = 1/ GHSV$)

1. Introduction

The environment protection is one of the main tasks of modern man. Now day at least everybody knows that, in a general way, the combustion of fossil fuels generates a big amount of harmful gases which damage the living part of the planet. Besides, natural fossil fuel reserves are getting to an end, so the finding of renewable clean energy sources which supply modern society energetic requirements must be a priority for preserving the human specie. Such alternative clean energy source could be the hydrogen fuel cells. For ethanol is a renewable energy source used as raw material to produce H₂ by the ethanol steam reforming reaction and subsequent application in hydrogen fuel cells, this work shows a deep study and a very detailed comparison among some catalysts that include some metals (Co, Ni, Cu, Zn) and supports (Al₂O₃, SiO₂) which have been already reported in the bibliography. The study of the effect of metal nature and the operation variables on conversion, yield, selectivity and catalyst stability allows to get some conclusions on the catalytic role of every active metallic specie in the ethanol steam reforming reaction pathway and to propose a general mechanism related to this reaction.

2. Results

2.1 Evolution of the catalytic role conception of some metallic species and supports more frequently used in the ESRR

2.1.1 It is necessary the proper doping of alumina with KOH to eliminate acidic sites from the surface and minimize the diethyl ether and ethene production.

- Nickel tends to form spinels with alumina at relatively high temperatures as well as copper (this last one at low concentrations). At loadings above 4% and forced by the presence of other oxides, copper is segregated to the surface as a CuO fase.

- Copper promotes the dehydrogenation much more than nickel at 300°C. In the copper presence and nickel absence a high dehydrogenation and no gasification was obtained, inversely a very low dehydrogenation and a poor gasification was obtained.

- Product quantitative distribution in ESRR doesn't depend on the catalyst's copper loading [1]

2.1.2 SiO₂ was almost inert toward ESRR ($X_{\text{EtOH}} < 10\%$). Al₂O₃ was active toward dehydration.

- Over ZnO carbon monoxide is not produced but C₂H₄, C₂H₆, CH₃COCH₃ [2]

2.1.3 Over Ni/La₂O₃ and Ni-La/Al₂O₃ with previous reductive treatment dehydrogenation at 300°C was observed. ESRR proceeded at $t > 400^\circ\text{C}$

- The presence of C₂H₄ and C₂H₆ is reported [3]

2.1.4 Selectivity toward ESRR follows the next order Co>Ni>Rh>Pt, Ru, Cu. Most of studied catalysts for ESRR are nickel-based catalysts with some addition of Co, Cr, Zn, K. It's generally accepted that nickel promotes the C-C bond rupture, the remaining metals' role is still discussed though.

- Over Ni-Cu/SiO₂ catalysts was found that in the range of 300-400°C dehydrogenation and methanation due to CO and CO₂ reaction with H₂ were the main reactions [4]

2.1.5 Over cobalt catalysts supported on several oxides such as SiO₂, Al₂O₃ y ZnO it was observed that:

- Over Co/Al₂O₃ ESRR was weak, dehydration was not weak. Dehydration is mainly related to the support's (Al₂O₃) acidic features. CO₂, CH₄, H₂ are reported as minor products.
- Over Co/SiO₂ the main reaction was dehydrogenation which is related to the support (SiO₂) dehydrogenation extension over Co/SiO₂ was higher than at using the support though. H₂, CO, CO₂, CH₄ and CH₃CHO are reported. C₂H₄ and C₂H₆ are also reported as minor products.
- Over Co/ZnO a high selectivity toward ESRR was achieved. CO is not reported, CH₃COCH₃ is.
- The cobalt aluminates formation is suspected.
- On ZnO and SiO₂ carbon deposition was observed, on Al₂O₃ it was not observed.
- On ZnO metallic cobalt is reported. Neither on SiO₂ nor on Al₂O₃ metallic cobalt is reported[5]

2.1.6 Over cobalt-based catalysts either supported on Al₂O₃ or SiO₂ an inhibitor role toward reduction after ESRR and even after pure H₂ treatment at 500 °C was observed This behavior is mainly related to the supports: Over Co/SiO₂ the main reaction took place was dehydrogenation, over Co/Al₂O₃ was dehydration.

- Over the rest of supports the reduced cobalt (metallic) amount depends only on the temperature under ESRR conditions.
- Catalyst was deactivated by carbides (Co₂C) formation [6]

2.1.7 Over Co/ZnO_{calc} (calcinated) the lowest catalytic performing was observed. Dehydrogenation was the main reaction at low temperatures while aldolic condensation was predominant at higher ones which is related to the support features.

- Over Co/ZnO_{red} (reduced) the main reaction was ESRR. CO and CH₄ were detected at low temperatures which can be due to ethanol decomposition to CO and CH₄. At higher temperatures CO was not detected which indicates it could react via WGS and methanation reactions
- The more the reduction degree increase, the more related to ESRR the catalyst is. It happen the same thing with the dispersion degree [7]

- 2.1.8 Iron-based and nanoscale produced catalysts supported on high surface alumina (M-Fe/Al₂O₃, M = Mo, Ni, Pd) have shown a high efficiency toward the decomposition of non diluted methane into hydrogen, the main problem is the coke deposition on the catalyst though.
- Acidic sites on alumina promote the ethane C-C bond rupture to yield ethene.
 - Binary catalysts should be reduced in order to generate metallic species capable of breaking C-C bonds [8]
- 2.1.9 Sodium loading, in the range of 0.06 to 0.98 percent, has a significant effect on the catalytic behavior of Co/ZnO. The more the sodium loading increase, the more the amount of sodium is segregated to the surface which avoid coke depositions, regulates the amount of produced acetaldehyde and diminish CO hydrogenation to CH₄ (methanation reaction). C₂H₄ is not reported [9]
- 2.1.10 Over Zn-Al-Cu catalysts, it was observed that zinc tend to form ZnAl₂O₄ spinel while copper appears just as a dispersed CuO fase. The higher the temperature is, the more the zinc segregation increase.
- The yield of H₂ y CO₂ does not depend on the copper loading
 - CH₄, C₂H₄ were detected. CO y CH₃COCH₃ were also detected since the bigining always as minor products
 - Acetaldehyde shows an intermediate behavior [10]
- 2.1.11 A kinetic study of the ESRR carried out without catalysts showed the presence of CH₄, CO, CO₂, C₂H₄ and CH₃CHO. A global reaction mechanism is proposed either in the absence or presence of water and many evidences are explained such as:
- Over copper dehydrogenation takes place but not the decomposition reaction, over nickel both reactions take place.
 - When using nickel a significant coke deposition observed. When copper is used, coke is not produced.
 - Acetic acid is only detected in the presence of water and over Cu sites.
 - Water dissociative adsorption through a red-ox mechanism which has already been reported for several Cu-Zn-Al catalysts used in the WGSR.

- The selectivity rise toward H₂ and CH₃CHO (approximately 20%) observed in the presence of water, the fact that acetic acid is not produced when copper is absent, the diminishing on the reformation products when water proportion increase and the catalyst stabilization because of water regeneration [11]

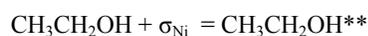
a. With water:



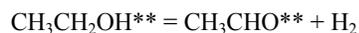
adsorption over Cu sites



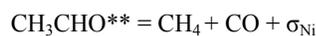
deshydrogenation



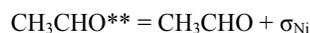
adsorption over Ni sites



deshydrogenation



C-C bond rupture

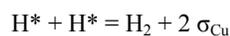
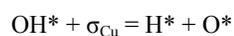
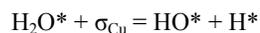


desorption

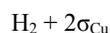
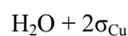
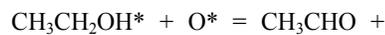
b. Without water:



adsorption over Cu sites



disociative adsorption



adsorptive oxidation

2.1.12 Over ZnO ethene, AcOEt and CH₃COOH were detected, CH₃COCH₃ was not detected. This results are attributed to the catalyst's acidic features [12]. A similar mechanism to the Mariño's [11] is proposed.

2.1.13 Over Cu-Zn-Al, usually used in the WGSR, dehydrogenation was the unique reaction at 300°C, at 400°C and above there were other products as CO₂, CH₃COCH₃, C₂H₄ and CH₄ traces.

- C₂H₄ is directly produced from CH₃CH₂OH

- CH₄ formation does not come from the CH₃CHO decomposition since CO is not among the reaction products.

- CO was not detected which could suggest direct WGSR nevertheless this reaction is not thermodynamically favoured at this temperature although this is the catalyst used in the

WGSR at low temperatures. Instead of this many authors have suggested the methyl formate formation and its later hydrolysis to CO₂ and H₂ [13]

- CO absence on some ZnO supported catalysts has been reported on Llorca's [2,5,6,7,9] works. In spite of this Barroso [10] reported presence of CO using this catalyst obtained via the citric acid technique without reduction steps.

2.1.14 As for alkaline metals (Li, Na, K) effect on activity, selectivity and stability of Ni/MgO catalyst toward ESRR it was concluded that Li is the most active one. The ESRR reaction is favoured when comparing to undoped catalyst [14]

2.1.15 Over Ni/Al₂O₃ H₂, CH₄, CO, CO₂ are reported. When the experiences were carried out with acetaldehyde and ethene H₂, CH₄, CO, CO₂ were reported. The ESRR product distribution for ethene is more favourable than for acetaldehyde [15]

2.1.16 Over Cu-Zn-Al and Ni-Zn-Al catalyst it was observed that Zn and Al mainly tend to form aluminates. ZnO, CuO, NiO are detected. Copper or nickel species were reduced to its metallic states either via reductive treatment or via ESRR. The spinel fase doesn't change under reductive atmosphere. H₂, CO₂, CH₄, CO, CH₃CHO, C₂H₄, CH₃COCH₃, propane, propylene and some other compound traces are detected [16]

2.2 Operation variables effect on conversión, yield, selectivity and stability.

2.2.1 Feed rate (R = H₂O/EtOH) effect

Almost all studies related to this variable belong to the group directed by **M. Laborde** in Argentina. It was found that there is a feed rate around 2.2, 3, 3.3, 3.5 (R_{mean} = 3) below which selectivity to intermediate and colateral products such as CH₃CHO, C₂H₄, CH₄, CO, CH₃COCH₃, other oxygenated products and hydrocarbons, the coke deposition and thus the catalyst poisoning increase suddenly. Over such feed rate selectivity toward collateral and intermediate products reach low and stable values. High feed rates also improve catalyst stability [4, 11, 13, 15]

- When $R = 0$, $Y_{\text{CH}_3\text{CHO}} = Y_{\text{H}_2} > Y_{\text{CH}_4} = Y_{\text{CO}}$ and acetic acid is not produced [11]

Possible reaction: $\text{CH}_3\text{CH}_2\text{OH} = \text{CO} + \text{CH}_4 + \text{H}_2$

- When $R = 1$ $Y_{\text{CO}_2} = Y_{\text{CH}_4}$ [15]

Possible reaction: $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} = \text{CH}_4 + \text{CO}_2 + 2\text{H}_2$

- When $R = 3.3$ Y_{CO} and Y_{CO_2} increase, Y_{C} and Y_{CH_4} diminish [15]

Possible reaction $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} = \text{CH}_4 + \text{CO}_2 + 2\text{H}_2$

and $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$

2.2.2 Temperature effect

It was found that in general form the more the temperature increase in the range of 300-500°C, the more the ethanol conversion increase as well as the selectivity toward H_2 and CO_2 and the more the selectivity toward acetaldehyde decrease [2, 4, 5, 6, 7, 11] Also in this range selectivity toward CO_2 increase at the expense of CO via WGS [12, 15] collateral products and methane decrease [4] and water conversion increase [15]

At temperatures up to 300°C the main reaction is dehydrogenation [1, 3, 4, 7, 9] In the range of 300-400°C carbon monoxide and CO_2 methanation is likely to occur [3, 4]. Above 500°C humid and dry (with CO_2) reformation of methane take place [3]

2.2.3 Residence time t_r ($t_r = 1/\text{GHSV}$) effect

It was found that if external diffusional resistances are present the more t_r decrease, the more the ethanol conversion increase as well as the selectivity toward ESRR products (H_2 and CO_2) Intermediate and collateral products selectivity (CH_3CHO , CH_4 , CO , CH_3COCH_3 , other oxygenated products and hydrocarbons) decrease while t_r decrease. Nevertheless this is true only until a minimum value below which the ethanol conversion decrease and appear some intermediates as CH_3CHO , CH_4 , CO . Either at too high or too low t_r values there will appear respectively intermediates and collateral products or intermediates products, will appear CO and the catalyst deactivation takes place [5, 6, 7]

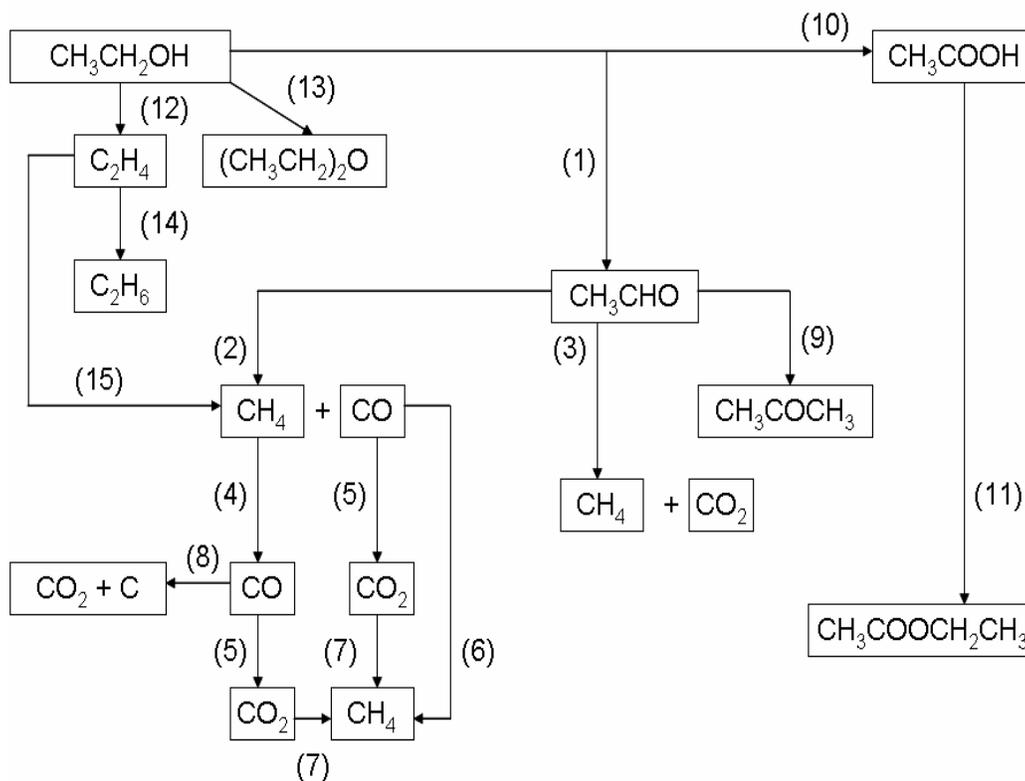
By the other hand when external diffusional resistances are absent the more t_r decrease below a minimum value, the more intermediate and collateral products increase in a suddenly way but above such value collateral products are minimized and intermediate products reach small and stable values. CO is also present in this conditions and deactivation takes place [3, 11, 12, 15]

2.2.4 Inert gases dilution effect

It was found that the more increase the rate $GI/(EtOH+H_2O)$, the more collateral and intermediate products decrease and the more the ESRR products selectivity increase. When ethanol conversion is not completed, acetaldehyde is also present [4, 5, 6, 7]

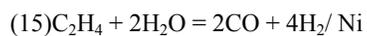
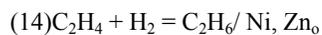
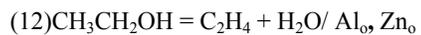
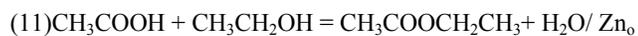
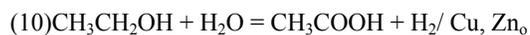
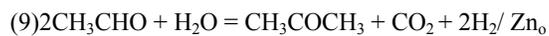
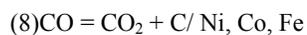
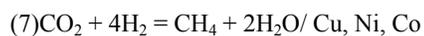
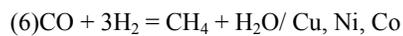
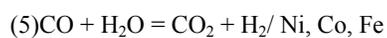
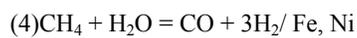
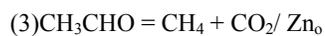
3. Discussion

3.1 It is possible to associate, based on the explicit information in the literature, the role of every single metal in the range of 300-500°C as though they were isolated over an “inert” support. Even in some cases there is possible, when ambiguities are absent, to associate such effect to the metal oxidation state according to the next diagram and the reaction set that follows it (M_o , oxidized metal; M_r , reduced metal; M there are ambiguities)



Diag. 1. Catalytic role of metallic species in the ESRR pathway.

Reaction set associated to the diagram



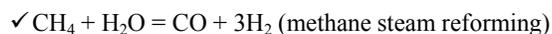
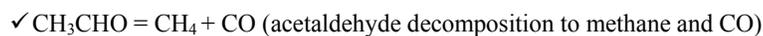
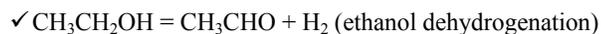
3.2 Copper is very active as for dehydrogenation. It is not a sole property for copper but for any metallic surface or oxides' basic groups such as ZnO (depends on the obtaining technique) and SiO₂ nevertheless breaking C-C bond is a specific feature of some of them such as Co, Ni, Zn.

3.3 Studied supports (SiO₂ and Al₂O₃) exert on Co, Ni, Zn and Cu an inhibitor role toward ESRR. SiO₂ is almost inactive (dehydrogenation takes place in some extent) whereas Al₂O₃ is very active in reactions related to its acidic features. As for Al₂O₃ it has been shown its tendency to form aluminates with these kind of transition metals. Its affinity follow the next order Zn > Ni > * Co > Cu

*there are ambiguities whether Ni > Co

3.4 Ethanol can be reformed without catalysts giving CH₄, CO, CO₂, C₂H₄ and CH₃CHO [11] Taking into account these products are produced in almost all catalysts under ESRR conditions and that when $R = 0$ $Y_{\text{CH}_3\text{CHO}} = Y_{\text{H}_2} > Y_{\text{CH}_4} = Y_{\text{CO}}$ [11] when $R = 1$ $Y_{\text{CO}_2} = Y_{\text{CH}_4}$, when $R = 3.3$ Y_{CO} and Y_{CO_2} increase, Y_{C} and Y_{CH_4} decrease [15] that it's almost generally accepted acetaldehyde is an intermediate and that methane reforming and WGSR take place in considerably extent in the range of 300-500°C [4, 12, 15] then it's possible to propose that ESRR traditionally represented as:

$\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} = 2\text{CO}_2 + 6\text{H}_2$ the chemical reaction of maximum H₂ yield and minimum CO yield could be actually a global chemical process of a small group of well known consecutive reactions (WGSR can be also collateral) which take place over almost all studied catalysts:



From this scheme it is evident that not only CH₃CHO is an intermediate but also CH₄ and CO. Obtaining different products and/or different quantities apart from those above when using different catalyst will indicate how far we are from the "ideal" process. From this point of view it

can be also proposed that every different step in the ESRR can be consecutively and separately optimized using the most convenient catalyst for each one and not necessarily only one catalyst for the whole process.

3.5 Poisoning or deactivation process with time on stream is a problem encountered in catalysts for ESRR, which is frequently associated with the presence of CO and coke deposition. It suggests CO could disproportionate into CO₂ and C via $\text{CO} = \text{CO}_2 + \text{C}$ (Boudouard coking). $\text{CO} + \text{H}_2 = \text{C(s)} + \text{H}_2\text{O}$ (CO reduction) and $\text{CH}_4 = \text{C(s)} + 2\text{H}_2$ (methane cracking) could be responsible too. It seems to be that working at or above $R = 3$, at relatively low t_r , dilution with inert gases and at high temperatures may minimize coke deposition. Some recent and attractive alternative to eliminate this problem is the use of alkaline metals as promoters which can also regulate the intermediates production such as acetaldehyde. They can also minimize some undesirable reactions such as methanation.

4. Conclusions

It is possible to separate the catalytic effect of every single metallic specie from the rest and thus assign to each one its own reaction pathway. Operation variables have a strong influence in the products distribution. Ethanol steam reforming could be a global chemical process of a small group of well known consecutive reactions: ethanol dehydrogenation, acetaldehyde decomposition to CH₄ and CO, methane steam reforming and WGS and thus every different step in the ESRR can be consecutively and separately optimized using the most convenient catalyst for each one and not necessarily only one catalyst for the whole process.

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