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HYDROGEN PRODUCTION BY ETHANOL STEAM REFORMING OVER A $NiAl_2O_4$ SPINEL DERIVED CATALYST

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SOMMARIO DEL RIASSUNTO

1. INTRODUZIONE

Negli ultimi anni il tema della sostenibilità ha acquisito sempre maggior importanza a livello globale, non solo in campo scientifico ma anche economico e sociale. Ne è un esempio l'Agenda 2030 per lo sviluppo sostenibile, un programma sottoscritto nel 2015 dai governi dei paesi membri dell'ONU, in cui tra gli obiettivi proposti vi è la lotta contro il cambiamento climatico. In particolare, il settimo obiettivo "Energia pulita e accessibile" punta ad assicurare a tutti l'accesso a sistemi di energia economici, affidabili, sostenibili e moderni. L'energia è un elemento fondamentale nella nostra vita e la sua richiesta è sempre maggiore: per questo è fondamentale trovare una fonte di energia sostenibile e rinnovabile che possa sostituirsi ai combustibili fossili. Petrolio, gas naturale e carbone continuano infatti ad essere le fonti principali per la sua produzione, causando emissioni di gas serra, inquinamento e consumando risorse non rinnovabili.

Come vettore energetico alternativo ai combustibili fossili, l'idrogeno è considerato un buon candidato. Ha un elevato potere calorifico (141,9 kJ/g), può essere utilizzato efficientemente per produrre elettricità in celle combustibili, la sua combustione ha come unico sottoprodotto l'acqua, può essere stoccato sotto forma di gas o liquido e può essere distribuito attraverso condotti. Il suo limite è che, nonostante sia l'elemento più abbondante nell'Universo, non è presente in natura in forma pura ed è necessario produrlo. La sua produzione oggigiorno non è però sostenibile, con il 96% dell'idrogeno derivante da fonti fossili non può essere considerata una soluzione alternativa rinnovabile e pulita.

Una possibile fonte pulita di idrogeno è l'etanolo. L'etanolo può infatti essere prodotto, sotto forma di bio-etanolo, attraverso la fermentazione di biomassa, in maniera rinnovabile e sostenibile; non contiene zolfo, è facile da trasportare, sicuro da stoccare e utilizzare, biodegradabile e poco tossico. Tra le diverse tecnologie che permettono di convertire l'etanolo in idrogeno, vi è il reforming catalitico con vapore, un processo termodinamicamente possibile che negli ultimi venti anni è stato ampliamente studiato.

1.1 Obiettivo

L'obiettivo di questa tesi è quello di studiare il reforming catalitico con vapore (steam reforming) di etanolo utilizzando come catalizzatore $NiAl_2O_4$ derivato da spinello e, in particolare, come temperatura, rapporto vapore/etanolo e tempo spaziale influiscono sulla reazione. La tesi si divide in due parti, una prima parte bibliografica in cui si riassume brevemente il processo, con e senza catalizzatore, e una seconda parte sperimentale in cui si discutono i risultati ottenuti utilizzando un catalizzatore $NiAl_2O_4$ derivato da spinello. La parte sperimentale è stata svolta presso la Facoltà di Scienza e Tecnologia di Leioa, appartenente all'Università dei Paesi Baschi (UPV-EHU).

La scelta del catalizzatore deriva dal fatto che la reazione è stata studiata in letteratura utilizzando ossidi del gruppo dello spinello a base di Ni senza un trattamento di riduzione previo. Questi studi hanno evidenziato che sono catalizzatori promettenti per il processo, mostrando un'alta conversione, una buona resa in H_2 e selettività a C_1 e stabilità nella struttura $NiAl_2O_4$ a causa della sua bassa riducibilità. (Muroyama et al, 2010). Questo studio tenta di comprendere il percorso di reazione del processo e le condizioni ottimali di questi catalizzatori, riducendoli però prima della reazione.

La reazione è stata analizzata in un reattore fluidizzato in un ampio range di condizioni operative (450-650°C, tempo spaziale fino a 0,2 $g_{catalizzatore}/(g_{EtOH}/h)$ e un rapporto vapore/etanolo da 3 a 9), con l'obiettivo di trovare la condizione che massimizzasse la produzione di idrogeno. È stata analizzata inoltre l'influenza del catalizzatore, all'interno del meccanismo generale e sulle singole reazioni, da cui dipenderà la distribuzione dei prodotti. Per l'analisi sono state calcolate la conversione di etanolo e la resa dell'idrogeno e dei prodotti carboniosi. In generale, dai risultati si evince che un aumento della temperatura del processo fino a 600°C favorisce sia la conversione dell'etanolo che la resa di idrogeno, mentre per temperature superiori le prestazioni peggiorano. Per avere una buona velocità di reazione è necessario un tempo spaziale minimo di 0,025 $g_{catalizzatore}/(g_{EtOH}/h)$ e in queste condizioni un aumento del rapporto acqua/etanolo nell'alimentazione è vantaggioso.

Altresì, si è studiata la deposizione di coke, concentrandosi sul tipo di carbonio prodotto e la causa che ha portato alla sua formazione. La quantità di coke depositato sopra il catalizzatore decresce con la temperatura e con il rapporto molare V/E ed è relativamente bassa per un valore di tempo spaziale ridotto. In questa reazione in particolare, si è dimostrata l'importanza della reazione di decomposizione dell'etilene, fonte principale della deposizione di carbonio, ma che non porta ad una completa disattivazione del catalizzatore. L'etilene porta infatti alla formazione di nanotubi di carbonio, che, se venduti, potrebbero essere una fonte di guadagno.

1.2 Termodinamica e meccanismi dello SRE

Il reforming con vapore dell'etanolo è un processo endotermico con la seguente stechiometria:

$$C_2H_5OH + 3H_2O \leftrightarrow 6H_2 + 2CO_2 \qquad \Delta H° = 173{,}4\ \mathrm{kJ/mol} \tag{1}$$

Per studiare come massimizzare la resa di idrogeno e la conversione di etanolo, è importante comprendere la termodinamica del processo. Il meccanismo di reazione è complesso a causa delle reazioni secondarie che avvengono in parallelo alla reazione principale e che generano prodotti intermedi e sottoprodotti, riducendo così la resa in H_2. Reazioni secondarie che possono verificarsi (Montero et al, 2017) e che sono interessanti per questo studio sono:

Deidrogenazione dell'etanolo	$C_2H_5OH \leftrightarrow C_2H_4O + H_2$	(2)
Disidratazione dell'etanolo	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	(3)
Decomposizione dell'acetaldeide	$C_2H_4O \rightarrow CH_4 + CO$	(4)
Reforming acetaldeide	$C_2H_4O + H_2O \rightarrow 2CO + 3H_2$	(5)
Reazione di Water Gas Shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	(6)
Steam reforming metano	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	(7)

Reazioni che producono coke e che contribuiscono alla disattivazione del catalizzatore sono:

Decomposizione dell'etilene	$C_2H_4 \rightarrow 2C + 2H_2$	(8)
Reazione di Boudouard	$2CO \leftrightarrow C + CO_2$	(9)
Decomposizione del metano	$CH_4 \rightarrow 2H_2 + C$	(10)

È stato ampiamente dimostrato in letteratura che, da un punto di vista termodinamico, lo steam reforming dell'etanolo si verifica sopra i 300 °C. In condizioni di equilibrio termodinamico e con un rapporto molare acqua/etanolo stechiometrico, i prodotti principali sono idrogeno, CO, CO_2 e metano e, in studi senza catalizzatore, con un intervallo di V/E di 3-9 e di temperatura di 500-700°C, non si osservano tra i prodotti né acetone né acido acetico (Montero et al, 2018). La conversione dell'etanolo e la selettività dell'idrogeno dipendono da temperatura, durata del processo, rapporto acqua/etanolo, tempo spaziale, tempo di contatto e presenza di O_2. Al fine di ridurre la concentrazione di sottoprodotti e aumentare la resa di idrogeno, è stato riscontrato che maggiori temperature e rapporto molare acqua/etanolo (nell'intervallo 4-10) migliorano le prestazioni del processo (Palma et al, 2012).

Il catalizzatore ha un ruolo cruciale in termini di conversione di etanolo, selettività e resa di idrogeno e la comprensione del suo meccanismo di reazione è fondamentale per la progettazione di un catalizzatore ottimale. In letteratura, il focus è quello di trovare un catalizzatore altamente attivo, stabile e resistente al coke. Diversi fattori influenzano l'attività e la stabilità del catalizzatore come la natura del metallo, il tipo di supporto, le condizioni di sintesi, il tipo di precursori, la presenza di additivi e le condizioni operative. La disattivazione del catalizzatore può portare alla perdita di attività catalitica e/o selettività nel tempo e per evitare che succeda sono state utilizzate diverse strategie, con modifiche al catalizzatore o alle condizioni operative.

In letteratura, è stato ampiamente studiato il tipo di fase attiva e di supporto (Hou et al, 2015). Rispetto alla fase attiva, i catalizzatori studiati nelle precedenti indagini possono essere generalmente classificati in due categorie: catalizzatori di metalli nobili e non nobili (Hou et al, 2015). L'osservazione generale è che i metalli nobili sono normalmente più attivi e selettivi dei metalli di transizione, ma sono anche più costosi.

Per quanto riguarda il supporto, se esiste, può interagire con l'etanolo e accelerarne la trasformazione, influenzando così l'attività del catalizzatore. La sua scelta, infatti, non solo influenza la reazione, ma può essere critica per la formazione di coke. Ad esempio, la γ-Al_2O_3, come supporto acido, è stata ampiamente utilizzata per la sua stabilità meccanica e termica e grazie alla sua elevata superficie specifica. Sfortunatamente, favorisce la disidratazione dell'etanolo per produrre etilene, precursore del coke, il quale alla lunga può portare a una significativa disattivazione del catalizzatore.

Tra i metalli nobili in fase attiva sono stati presi in considerazione Rh, Ru, Pt, Pd e Ir, tra quelli non nobili principalmente i metalli di transizione Ni e Co. Il catalizzatore a base Ni ha mostrato la migliore attività, con elevate conversioni dell'etanolo e selettività a idrogeno. Tuttavia, il Ni è meno attivo per la reazione WGS (Water Gas Shift) e i suoi problemi sono legati principalmente alla formazione di coke e alla sinterizzazione ad alte temperature, che portano a un peggioramento delle prestazioni nel tempo.

1.3 Effetto delle condizioni operative

La temperatura ha un effetto importante sul meccanismo di reazione, sulla conversione, sulla selettività e sulla stabilità del catalizzatore. Studi riguardanti la reazione non catalizzata (usando CSi come unico solido nel reattore) hanno dimostrato che la conversione dell'etanolo è irrilevante fino a 500 °C (Vicente et al, 2014a). La temperatura ottimale della reazione catalitica dipende invece dal tipo di catalizzatore utilizzato e può avvenire a temperature più basse. Da un lato la reazione è endotermica e quindi è favorita ad alta temperatura e un aumento della temperatura impedisce la formazione di metano, considerato uno dei principali sottoprodotti (Hou et al, 2015). Dall'altro lato, ad alta temperatura (>600°C) può aver luogo la sinterizzazione del metallo, la richiesta di energia è maggiore e la reazione di WGS, che aumenta la resa di H_2 e diminuisce quella di CO, è sfavorita (il verificarsi della reazione di WGS passa per un massimo).

A basse temperature è presente un'ampia gamma di sottoprodotti indesiderati come composti ossigenati e idrocarburi (Mattos et al, 2012), mentre a temperature più elevate aumenta la conversione dell'etanolo e le reazioni di reforming sono più favorevoli, il che si traduce in una maggiore resa in H_2, CO, CO_2 e CH_4.

Per quanto riguarda la quantità di acqua nell'alimentazione, la reazione è stata studiata in letteratura utilizzando rapporti molari acqua-etanolo compresi tra 1 e 15. In generale, è stato riscontrato che un aumento del quantitativo di acqua aumenta la conversione dell'etanolo e la resa in idrogeno (Hou et al, 2015). Per quanto riguarda gli altri prodotti, si è visto che, aumentando il rapporto V/E, si riducono anche le velocità di formazione di sottoprodotti come etilene e acetaldeide, aumenta anche la produzione di CO_2 e diminuisce quella di CO. Tuttavia, l'aggiunta di grandi quantità di acqua implica maggiori costi operativi che devono essere presi in considerazione.

Per le reazioni catalitiche anche il tempo spaziale è un fattore da prendere in considerazione. Il tempo spaziale è definito come il peso del catalizzatore diviso per la portata di etanolo. In generale, un aumento del tempo spaziale riduce la formazione di prodotti intermedi e migliora la conversione dell'etanolo e la selettività dell'idrogeno (Hou et al, 2015).

1.4 Disattivazione del catalizzatore

Uno dei problemi principali dello steam reforming catalitico dell'etanolo è la stabilità del catalizzatore, che deve essere presa in considerazione durante la sua progettazione. In articoli precedenti, sono stati evidenziati quattro meccanismi di disattivazione del catalizzatore la cui entità dipende dalle condizioni operative e dal catalizzatore utilizzato: formazione di coke, sinterizzazione (che può avvenire nei catalizzatori di metalli di transizione quando si utilizzano alte temperature e rapporti molari vapore/etanolo elevati), ossidazione e avvelenamento del metallo (Hou et al, 2015). La deposizione di coke può distruggere la struttura del catalizzatore e occupare la sua superficie, riducendo considerevolmente la sua attività, causando una perdita di selettività dell'idrogeno e di conversione dell'etanolo. In letteratura (Vicente et al. 2014a) l'origine del coke è stata attribuita a tre principali cause: disidratazione dell'etanolo sui siti acidi del catalizzatore seguita da polimerizzazione dell'etilene, reazione di Boudouard, e decomposizione di metano.

La temperatura gioca un ruolo importante nella deposizione di coke poiché influenza il percorso di reazione e la quantità totale di carbonio depositato diminuisce all'aumentare della temperatura di reazione. Anche per quanto riguarda il rapporto molare acqua/etanolo, un aumento di V/E porta a una diminuzione del coke prodotto. Le proprietà acido/base del supporto influenzano la stabilità del catalizzatore (Mattos et al, 2012): il supporto di Al_2O_3, utilizzato per la sua elevata superficie e stabilità, a causa della sua acidità favorisce la formazione di etilene, precursore del coke.

In bibliografia si sono distinti due tipi di coke: il coke incapsulante e il coke filamentoso. Il primo ha natura amorfa e blocca i siti metallici; si forma per polimerizzazione dell'etilene, e per questo motivo è favorito dalla presenza di siti acidi nel supporto. Quello filamentoso, invece, è strutturato in fibre e non influisce sulla disattivazione tanto quanto il primo (Mattos et al, 2012). Il catalizzatore, infatti, può rimanere attivo durante la reazione nonostante una notevole quantità di carbonio depositato sopra le particelle, poiché i filamenti ricoprono il catalizzatore ma non ostacolano l'adsorbimento dell'etanolo che avviene nelle porosità (Montero et al, 2015). Il tipo di carbonio accumulato dipende dalla natura del metallo attivo utilizzato e dalle condizioni di reazione.

La deposizione di coke è generalmente considerata un fattore negativo, ma la formazione di un certo tipo di carbonio sulla superficie del Ni qualche volta può essere positiva, aumentando la stabilità e l'attività del catalizzatore. Molti ricercatori hanno scoperto che il carbonio filamentoso formato durante il processo di steam reforming con catalizzatore a base Ni, ha la forma di nanotubi di carbonio (CNT) (Quan et al, 2019). Questo materiale sta acquisendo interesse grazie alle sue particolari proprietà fisiche e chimiche e la sua vendita potrebbe dare un valore economico aggiunto alla produzione di H_2 tramite il reforming catalitico a vapore dell'etanolo.

2. PARTE SPERIMENTALE

La parte sperimentale è stata portata avanti presso i Laboratori del Dipartimento di Ingegneria Chimica della Facoltà di Scienze e Tecnologie (a Leioa) dell'Università dei Paesi Baschi (UPV-EHU). Lo scopo dello studio era capire come le condizioni operative influenzassero la reazione di steam reforming utilizzando un catalizzatore derivato da spinello $NiAl_2O_4$ al fine di trovare i valori ottimali di temperatura, tempo spaziale e rapporto molare V/E.

2.1 Preparazione e caratterizzazione del catalizzatore

Il catalizzatore $NiAl_2O_4$ è stato preparato attraverso il metodo di co-precipitazione, utilizzato da Arandia et al (2020). Si parte da idrossido di ammonio (NH_4OH 0,6 M) come agente precipitante, che si aggiunge a una soluzione di $Ni(NO_3)_2 \cdot 6H_2O$ e $Al(NO_3)_2 \cdot 9H_2O$ fino a raggiungere un pH di 8. La miscela viene poi filtrata, lavata con acqua e la parte filtrata si pone in stufa per 24 h a 110°C e si calcina a 850°C per 4 h con una rampa di 10°C/min. Una volta calcinata, si macina fino a ottenere dei grani di 0,15-0,25 mm. La dimensione della particella di Ni influenza la reazione: aumentando la dimensione delle particelle di Ni attivo a 25-30 nm, la resa di H_2 diminuisce e si favorisce la formazione di coke.

Prima della reazione, il catalizzatore si riduce in situ utilizzando un flusso di idrogeno di 10 ml/min e uno di azoto di 135 ml/min a 850°C con una rampa di 10°C/min. Queste condizioni assicurano la completa riduzione dello spinello $NiAl_2O_4$ con una buona dispersione delle particelle di Ni^0 sul supporto Al_2O_3.

Per identificare le fasi cristalline e studiare la morfologia si è effettuata un'analisi con diffrazione di raggi X. Le Fig. 1 a e b mostrano le curve di diffrazione (XRD) per il catalizzatore ossidato e ridotto rispettivamente.

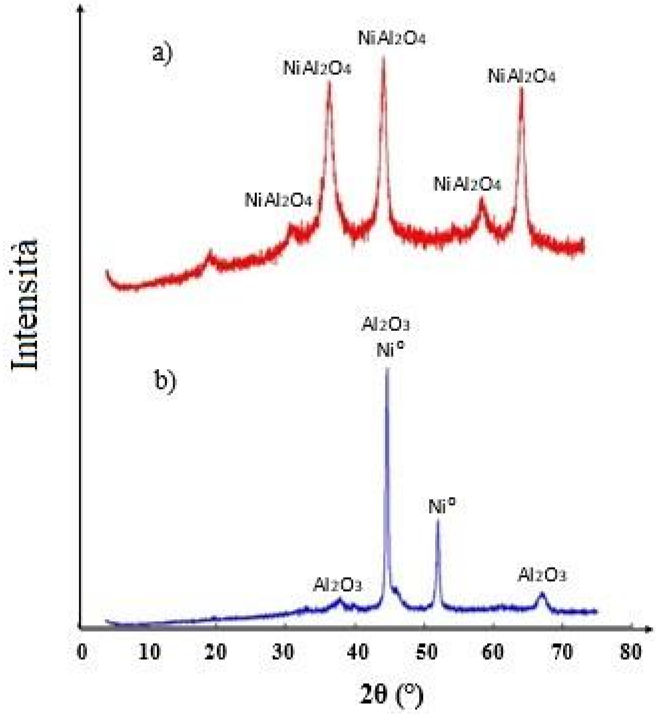

Figura 1: Curve di diffrazione XRD per il catalizzatore ossidato (a) e ridotto (b)

La curva che corrisponde al catalizzatore ossidato (Figura 1a) mostra picchi che corrispondono alla tipica struttura cubica prevista per questo spinello, a 2θ = 31,2 -37- 45,1- 59,7 e 65,6°, mentre non si rilevano linee di diffrazione corrispondenti a fasi segregate di Al_2O_3. Riducendo la struttura dello spinello $NiAl_2O_4$, la curva del catalizzatore ridotto (Figura 1b) mostra picchi a 2θ = 44,65 e 51,95° corrispondenti a cristalli di Ni ridotti e a 2θ = 37-44,65 e 67,14°

corrispondenti alla fase Al_2O_3. Ciò indica che il processo di riduzione a 850 ºC converte completamente lo spinello $NiAl_2O_4$ in cristalli di Ni supportati su Al_2O_3 (Ni/Al_2O_3). Utilizzando l'equazione di Scherrer si è stimata la dimensione media dei cristalli di Ni ridotti usando il picco di diffrazione a $2\theta = 51{,}95^{\circ}$, ottenendo una dimensione media di 26 nm.

2.2 Sistema di reazione

Le prove cinetiche sono state condotte in un reattore isotermico a letto fluidizzato (22 mm di diametro interno e lunghezza totale di 460 mm) collegato in linea a un gascromatografo per l'analisi del prodotto. Il catalizzatore è stato miscelato con un solido inerte (CSi, granulometria 105 µm) in modo da ottenere un buon regime di fluidizzazione e come alimentazione è stata utilizzata una miscela di etanolo, acqua, azoto in fase gas. La portata è stata regolata in modo da avere nell'alimentazione una composizione molare di etanolo del 5% e il rapporto V/E desiderato. I composti sono stati quantificati e identificati utilizzando standard di calibrazione a concentrazione nota.

Le prestazioni del catalizzatore sono state studiate per diverse condizioni operative di temperatura, rapporto molare vapore/etanolo e tempo spaziale e con una pressione totale di 1,7 bar. L'intervallo di temperatura era compreso tra 450 e 650°C ma la reazione è stata studiata principalmente per temperature di 500 e 600°C. Il rapporto V/E studiato era pari a 3, 6 e 9 e l'intervallo di tempo spaziale compreso tra 0,0075 e 0,2 $g_{catalizzatore}/(g_{EtOH}/h)$.

Per poter confrontare le prestazioni del catalizzatore nelle diverse condizioni operative sono state calcolate la conversione dell'etanolo e le rese dei prodotti per ciascuna reazione.

Al fine di valutare la quantità di carbonio che non era presente nella corrente gassosa in uscita e quindi era sotto forma di carbonio solido depositato, sono state calcolate le moli di C in ingresso e in uscita. Inoltre, al termine di ogni reazione, è stato pesato il catalizzatore e la quantità di carbonio depositato sul catalizzatore è stata calcolata sottraendo il peso iniziale del catalizzatore da quello finale.

3. RISULTATI

3.1. Effetto delle condizioni operative

3.1.1 Temperatura

Per quanto riguarda la temperatura, vogliamo le migliori prestazioni utilizzando la temperatura più bassa possibile, in modo da abbassare i costi di riscaldamento. Come si può osservare da Tabella 1, la resa di idrogeno e la conversione di etanolo per un tempo spaziale di 0,025 $g_{catalizzatore}/(g_{EtOH}/h)$ e un V/E di 3 aumentano con l'aumentare della temperatura. A 450°C la conversione dell'etanolo è già elevata (0,8), e dopo 500°C è quasi completa.

Tabella 1: Conversione etanolo e resa di idrogeno in funzione della temperatura per un tempo spaziale di 0,025 $g_{catalizzatore}/(g_{EtOH}/h)$ e un V/E di 3

Temperatura (°C)	450	500	550	600	650
Conversione EtOH	0,821	0,983	0,990	0,996	0,981
Resa idrogeno	0,278	0,346	0,379	0,448	0,389

Nell'intervallo di temperatura 500-600 °C (Figura 2) si ha un aumento della resa in CO_2, C_2H_4 e CO, mentre diminuisce la resa in metano.

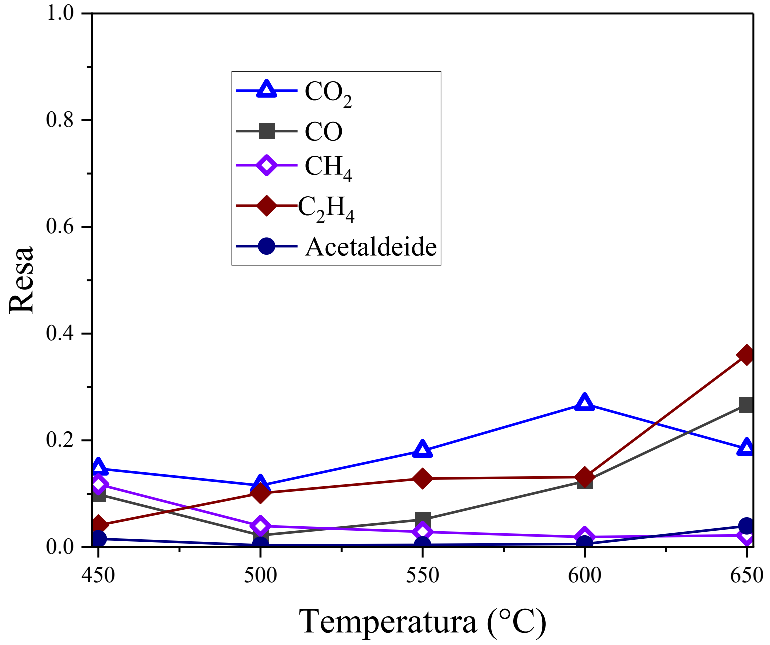

Figura 2: Resa dei prodotti carboniosi in funzione della temperatura con un V/E di 3, un tempo spaziale di 0,025 $g_{catalizzatore}/(g_{EtOH}/h)$.

Ciò è probabilmente dovuto al fatto che un aumento della temperatura in questo intervallo favorisce le reazioni di disidratazione dell'etanolo (Eq. 3), WGS (Eq. 6) e steam reforming di metano (Eq. 7). In particolare, la resa di metano diminuisce quasi linearmente con la temperatura e contemporaneamente aumenta una resa di CO, dimostrando l'importanza ad alte temperature della reazione (endotermica) dello steam reforming di metano (Eq. 15).
La resa di C_2H_4 aumenta con la temperatura e ciò è dovuto al fatto che l'etilene è un prodotto di reazione primario e la reazione di decomposizione dell'etilene (in H_2 e carbonio) è sfavorita a temperature maggiori. La quantità di acetaldeide prodotta è bassa nell'intervallo di temperatura 450-600°C, dimostrando che per queste temperature la deidrogenazione dell'etanolo (Eq 2) avviene in misura ridotta.

Per temperature più elevate (650°C) le rese di CO_2 e H_2 diminuiscono mentre aumentano quelle di CO, C_2H_4 e acetaldeide. A questa temperatura il meccanismo di reazione è differente, si favoriscono la deidrogenazione (Eq 2) e la disidratazione (Eq 3) dell'etanolo per cui nei prodotti si può trovare l'acetaldeide mentre viene sfavorita la decomposizione dell'etilene in idrogeno e carbonio.

La temperatura non influenza solo il meccanismo di reazione, ma anche la stabilità del catalizzatore nel tempo. Per bassi valori di tempo spaziale, nel range di temperatura 500-600°C, dopo un certo tempo la resa a idrogeno diminuisce e contemporaneamente quella a etilene aumenta. Questo è dovuto al fatto che all'inizio l'etilene si forma ma è presente come intermedio di reazione, decomponendosi rapidamente in idrogeno e carbonio. Dopo un certo periodo però il coke depositato sul catalizzatore porta ad una sua parziale disattivazione: la reazione che porta alla formazione di etilene continua ad avvenire ma successivamente non si decompone a idrogeno e carbonio. Questo periodo è più lungo per temperature più basse e ciò è probabilmente dovuto al fatto che a temperature più elevate la reazione di decomposizione dell'etilene è più rapida, il carbonio si forma più velocemente e quindi la disattivazione della reazione è più rapida.

Per temperature superiori a 600°C la conversione diminuisce con il tempo di funzionamento. È possibile che ad alta temperatura, la reazione di formazione dell'acetaldeide attraverso la deidrogenazione dell'etanolo sarebbe responsabile della formazione di un coke amorfo e incapsulante, che porta a una rapida disattivazione per le reazioni che avvengono sia sui siti metallici che sui siti acidi del supporto (Montero et al., 2018).

3.1.2 Rapporto molare V/E

Per valori di tempo spaziale elevati, Tabella 2, all'aumentare della quantità di acqua la resa a idrogeno aumenta. Vengono favoriti il reforming di CH_4 e la reazione di WGS mentre è sfavorita la reazione di metanazione, con un aumento quasi lineare delle rese di CO_2 e H_2 e una diminuzione in quelle di CO e CH_4 (Figura 3).

Tabella 2: Conversione etanolo e resa in idrogeno per una temperatura di 600°C e un τ di 0,1 $g_{catalizzatore}/(g_{EtOH}/h)$ in funzione del rapporto V/E

V/E	3	6	9
Conversione EtOH	1	0,996	0,996
Resa idrogeno	0,452	0,561	0,709

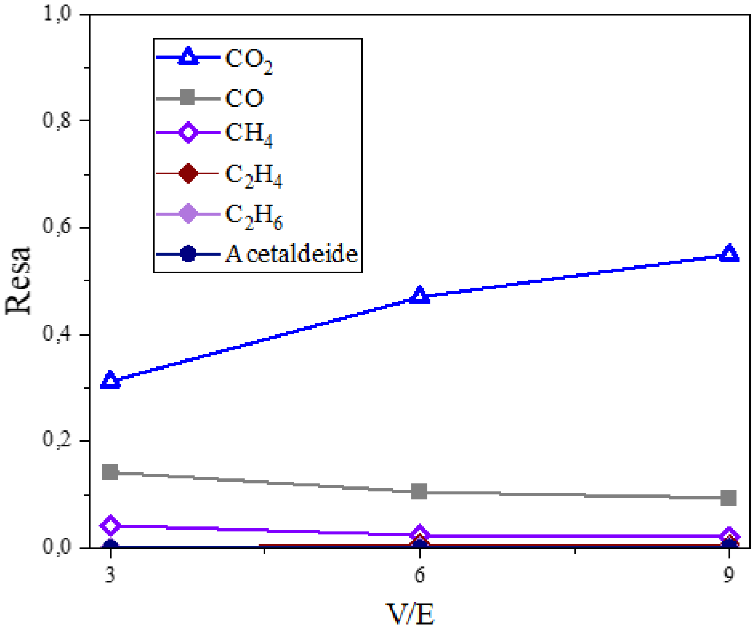

Figura 3: Resa dei prodotti carboniosi in funzione del rapporto V/E, con una temperatura di 600°C, un tempo spaziale di 0,1 $g_{catalizzatore}/(g_{EtOH}/h)$.

Per valori di tempo spaziale bassi invece (regime cinetico) la resa di idrogeno rimane pressoché costante con il rapporto molare V/E, mentre la conversione diminuisce (Tabella 3). Questa tendenza è dovuta al fatto che l'acqua, in regime cinetico, ha un effetto inibitore sulla cinetica complessiva, mentre non influenza il meccanismo di reazione, con rese dei prodotti che rimangono costanti nell'intervallo V/E studiato.

Tabella 3: Conversione etanolo e resa in idrogeno per una temperatura di 600°C e un τ di 0,01 $g_{catalizzatore}/(g_{EtOH}/h)$ in funzione del rapporto V/E

V/E	3	6	9
Conversione EtOH	0,968	0,942	0,826
Resa idrogeno	0,215	0,235	0,197

Anche per quanto riguarda la stabilità del catalizzatore l'influenza del rapporto V/E dipende se si lavora in regime cinetico o termodinamico. In regime termodinamico il catalizzatore nelle 4 h di reazione non si disattiva e quindi il rapporto molare V/E non influisce sulla conversione dell'etanolo e sulla resa dei prodotti, che rimangono costanti nel tempo di reazione. Questo non è vero quando si lavora in regime cinetico: per valori di V/E maggiori la resa dei prodotti e la conversione dell'etanolo rimangono stabili nel tempo mentre quando la quantità di acqua è minore, la reazione di decomposizione dell'etilene viene disattivata più rapidamente, il che porta ad una resa di idrogeno inferiore rispetto a quella all'inizio della reazione.

3.1.3 Tempo spaziale

Un altro parametro che influenza il processo è il tempo spaziale, definito come il peso del catalizzatore diviso per la portata di etanolo. La resa di idrogeno aumenta all'aumentare del tempo spaziale e l'incremento è maggiore quando il tempo spaziale a 500°C è inferiore a 0,05 $g_{catalizzatore}/(g_{EtOH}/h)$ (Tabella 4). La conversione è completa a 0,05 $g_{catalizzatore}/(g_{EtOH}/h)$ a 500°C e a 0,025 $g_{catalizzatore}/(g_{EtOH}/h)$ a 600°C.

Tabella 4: Conversione etanolo e resa di idrogeno a T=500°C e V/E di 3 in funzione del tempo spaziale

τ ($g_{catalizzatore}/(g_{EtOH}/h)$)	0,01	0,025	0,05	0,1	0,2
Conversione EtOH	0,9	0,977	0,991	0,996	0,997
Resa idrogeno	0,273	0,333	0,363	0,4	0,4

Il tempo spaziale influenza la stabilità del catalizzatore. Per valori di tempo spaziale più bassi, la resa a etilene è elevata e poi diminuisce. Questo perché l'etilene è un intermedio che si forma rapidamente per disidratazione dell'etanolo (Eq 3) e poi si decompone rapidamente in idrogeno e carbonio a valori di tempo spaziale più elevati. Per valori di tempo spaziale maggiori di 0,1 $g_{catalizzatore}/(g_{EtOH}/h)$ invece la resa dell'etilene non varia nel tempo nelle prime 4 h di reazione.

L'acetaldeide viene rilevata solo per i valori di tempo spaziale più bassi, dimostrando che si forma durante la reazione ma come intermedio e che reagisce rapidamente, probabilmente formando CO_2. Al contrario, le rese di CO_2, CH_4, CO e H_2 aumentano, poiché la velocità delle reazioni intermedie aumenta, e gli intermedi si convertono rapidamente a prodotti finali.

3.2 Effetto del coke depositato

Uno dei problemi principali con il catalizzatore a base di Ni per la reazione di steam reforming dell'etanolo è la disattivazione dovuta alla deposizione di coke (Wang, 2009). Inoltre, il supporto acido è molto attivo per la reazione di disidratazione dell'etanolo (Eq 3) e per questo motivo vi è un'elevata produzione di etilene, una delle principali cause di deposizione di coke utilizzando questo catalizzatore. All'inizio, quando il catalizzatore è fresco, la formazione dell'etilene è seguita dalla decomposizione dell'etilene (Eq 18) con formazione di idrogeno e coke. Questo coke provoca una disattivazione parziale del catalizzatore che non è più attivo per la reazione di decomposizione dell'etilene, con conseguente diminuzione della resa in idrogeno nel tempo.

La reazione di decomposizione dell'etilene avviene all'inizio della reazione, ed è maggiormente favorita a bassa temperatura, prima che si disattivi e non produca più coke. Per questo motivo la quantità di coke depositato sul catalizzatore diminuisce all'aumentare della temperatura. La quantità di coke prodotta a 650°C è minore ma ha un percorso di formazione diverso.

La formazione di coke diminuisce con il rapporto V/E, sia per il regime cinetico che termodinamico, mentre per quanto riguarda l'andamento con il tempo spaziale non ha un andamento monotono.

4. CONCLUSIONI

Il catalizzatore $NiAl_2O_4$ derivato da spinello ridotto a 850 °C si è dimostrato molto attivo per la reazione SRE, con una conversione dell'etanolo quasi completa (per temperature superiori a 500 °C e tempo spaziale superiore a 0,025 $g_{catalizzatore}/(g_{EtOH}/h)$) e una buona resa di idrogeno.

La temperatura è la condizione che più influenza la selettività della reazione. Da questo studio sperimentale possiamo concludere che l'intervallo di temperatura con le migliori prestazioni per questo catalizzatore è 500°C-600°C. Questo perché un aumento della temperatura favorisce la disidratazione dell'etanolo, la reazione di WGS e il reforming con vapore di metano, portando a una maggiore conversione di etanolo e produzione di idrogeno. A temperature più elevate, tuttavia, l'equilibrio della reazione WGS si sposta verso sinistra, portando a prestazioni scadenti. L'aumento del rapporto molare V/E ha un effetto benefico sulla conversione e sulla produzione di idrogeno, e il suo effetto è maggiore a basso valore del rapporto molare V/E, mentre da 6 a 9 non influisce molto. Aumentando la quantità di acqua aumenta anche il costo dell'operazione; quindi, sarebbe necessario studiare il processo da un punto di vista economico per scegliere il valore ottimale.

È necessario un tempo spaziale superiore a 0,1 $g_{catalizzatore}/(g_{EtOH}/h)$ non solo per avere una buona conversione, ma anche per la stabilità del catalizzatore. Infatti, con un basso valore di tempo spaziale il catalizzatore si disattiva rapidamente e l'etilene non reagisce formando idrogeno.

Per avere prestazioni migliori (maggiore resa di H_2, conversione completa dell'etanolo, buona stabilità del catalizzatore), si raccomandano le seguenti condizioni operative: 600 °C, tempo spaziale superiore a 0,1 $g_{catalizzatore}/(g_{EtOH}/h)$ e rapporto molare V/E = 9. Sotto queste condizioni si ottiene una resa di H_2 del 74%, che rimane elevata durante il tempo in esercizio.

Inoltre, la deposizione di coke non incide molto sulle prestazioni del catalizzatore che non viene disattivato completamente e si trova sotto forma di CNT che possono avere un interesse commerciale.

Il catalizzatore derivato dallo spinello $NiAl_2O_4$ ridotto a 850°C in generale ha buone prestazioni per SRE. Tuttavia, dopo esser stato utilizzato, non è possibile rigenerarlo. Per questo motivo sono necessari ulteriori studi su come evitare questo fenomeno.

TABLE OF CONTENTS

SUMMARY

In this work the reaction of steam reforming of ethanol to produce hydrogen using a $NiAl_2O_4$ spinel catalyst has been studied, focusing in particular on how temperature, steam to ethanol ratio and space time influence the reaction. The first part of the thesis focuses on the literature related to the reaction, using different types of catalyst, while the second refers to the experimental study using a $NiAl_2O_4$ spinel derived catalyst. The experimental part has been carried out at the Faculty of Science and Technology, in Leioa, belonging to the University of the Basque Country (UPV-EHU).

The steam reforming of ethanol over a $NiAl_2O_4$ spinel catalyst was analyzes in a fluidized bed reactor under a wide range of operating conditions (450-650 °C, space time up to 0.2 $g_{catalyst}/(g_{EtOH}/h)$, and steam/ethanol (S/E) molar ratio in the feed between 3 and 9) in order to select optimum conditions for maximizing H_2 production. The significance that the individual reactions in the reaction mechanism has on products distribution and the role of the catalyst in the extent of these reactions has also been analyzed. For the analysis, ethanol conversion and the yield of hydrogen and carbonaceous products were calculated. It has been showed that increasing the temperature of the process favors both ethanol conversion and hydrogen yield until 600 °C, while for higher temperature the results are worst. In order to have a proper rate of reaction a space time of 0.025 $g_{catalyst}/(g_{EtOH}/h)$ is needed and in thermodynamic regime an increase in water quantity leads to better performance.

Moreover, coke deposition on the catalyst was analyzed, focusing on the type of coke produced and how it is formed. The quantity of coke deposited on the catalyst decreases with temperature and S/E molar ratio and is relatively low for low value of space time. In particular, the importance of ethylene decomposition reaction as the main source of carbon deposition has been showed, that however does not lead to a strong deactivation of the catalyst. In fact, it has been found out that ethylene is an important precursor for the formation of carbon nanotubes, that doesn’t lead to complete catalyst deactivation and can be an interesting product for the market.

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1. INTRODUCTION

This study is inserted in a bigger field, that of sustainability and searching for new energy sources that do not derive from fossil fuels. Finding alternative and renewable energy sources is an issue that is becoming more and more important nowadays, both for environmental issues linked to the global warming, but also to replace fossil fuels that are no renewable sources and their quantity is rapidly decreasing. These goals cover not only the environmental but also the economic and social sphere and for this reason are one of the main objectives of studies in the field of chemical engineering. Both the Polytechnic University of Turin and the University of Bilbao have carried out a lot of their research and studies in this direction.

As an alternative to fossil fuels, the hydrogen can be a good candidate as energy carrier. The problem is that, at present, the most comprehensive process for the generation of hydrogen-rich syngas is endothermic catalytic steam reforming (SR) of light hydrocarbons. Most often, the feed is natural gas, (Abdin, 2020) that is not a renewable source. A good solution would be the production of hydrogen from the steam reforming of ethanol (SRE) using bioethanol, a prosperous renewable energy carrier mainly produced from biomass fermentation (Ogo and Sekine, 2020). To make this route feasible, the process has been largely studied in the last years and in the literature lot of works can be found in which different operating conditions and catalysts are used (Contreras et al, 2014) (Tengfei et al, 2015) (Ogo and Sekine, 2020). Especially the focus of these studies was on the catalyst used to carry out the reaction, since catalysts play a crucial role in the reactivity toward complete conversion of ethanol. Each catalyst induces different pathways, selectivity, yield and, therefore, the selection of a suitable catalyst plays a vital role in ethanol steam reforming for hydrogen production.

In Fig 1, the number of publications by year when searching ‘steam reforming of ethanol’ on Scopus is showed. As we can see the literature linked to SRE, since 2005, is rich, and the University of Basque Country UPV EHU contributed to it.

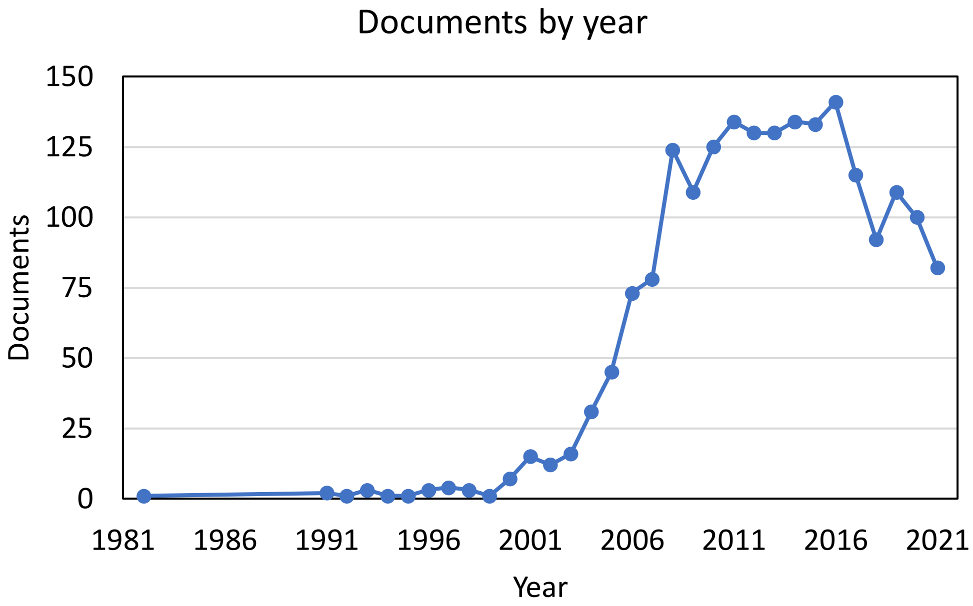

Figure 1: Number of publications by year searching 'ethanol steam reforming' on Scopus, 1 June 2021.

1.1. Sustainability and renewable energy

In recent years, the theme of sustainability has become more and more important, embracing various fields including economic, social, and scientific and entering into everyday life.

A prime example of this is the 2030 agenda for sustainable development, an action program for people, planet and prosperity signed in September 2015 by the governments of the 193 UN member countries. It incorporates 17 Objectives for Sustainable Development - Sustainable Development Goals, Sdgs – that are common objectives on a set of important issues for development such as the fight against poverty, the eradication of hunger and the fight against climate change. Among these objectives, the United Nations' Sustainable Development Goal 7i (SDG 7) recognizes that combining renewables and efficiency provides integrated means towards achieving sustainable energy access for all. Energy production and use account for more than two-thirds of global greenhouse gas emissions. Taken together, renewable energy deployment and energy efficiency measures can potentially achieve most of the carbon reductions required to keep global temperature rise below 1.5 degrees Celsius.

Figure 2: 17 Sustainable Development Goals, Sdgs of the 2030 agenda for sustainable development (modified image)

Energy is now a fundamental element in our everyday life, with an ever-increasing demand. The current annual world energy demand, as cited by the U.S. Energy Information Administration, is 590 quadrillion British Thermal Units (BTUs). The major contributors to this energy include oil, natural gas, and coal attributing nearly 82% of the total world energy supply (Nanda et al, 2017). The massive use of fossil fuels as energy source has caused serious environmental problems such as air pollution and greenhouse gas emissions and its amount is not infinite, with an uncertainty in fossil fuel prices and crude oil future supply chain. For these reasons it is urgent to move towards the use of renewable energy sources, such as solar, wind, geothermal, hydropower and the use of biomass. Modern bioenergy provided 5.1% of total global final energy demand in 2018, accounting for around half of all renewable energy in final energy consumption. The aim is to find alternative energy sources that can be environmentally sustainable, affordable, reliable and not toxic (Nanda et al, 2017).

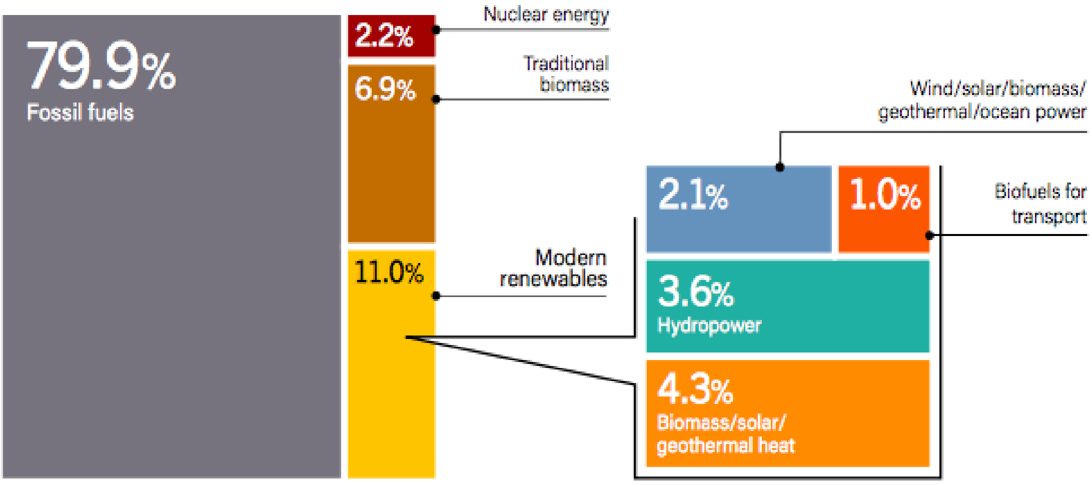

Figure 3: Estimated Renewable share of Total Final Energy Consumption, 2018 from Renewable 2020 Global status report.

1.2. Ethanol as a sustainable source for hydrogen production

The choice of using ethanol as a source to produce hydrogen is due to various factor. First, ethanol is easy to transport, safe to storage and handle, biodegradable and less toxic than methanol (Nanda et al, 2017).

It could be easily decomposed in the presence of water to generate a hydrogen-rich mixture and it is free from catalyst poisons such as sulfur (Haryanto et al, 2005). It can be produced renewably by fermentation of biomass sources, such as energy plants, agroindustry wastes, forestry residue materials, and organic fraction of municipal solid waste, the so-called bio-ethanol, that is considered to be a mature technology (Contreras et al, 2014). Recently the conversion of ethanol to hydrogen through hydrothermal, electrochemical, photochemical and thermochemical technologies has been studied (Nanda et al, 2017).

The choice to produce hydrogen is that it has been identified as an advanced alternative fuel, energy vector and energy carrier to support sustainable energy development. This is because it can be used in a fuel cell to generate electricity with high efficiency, it burns cleanly as the only by-product is water, can be stored as a liquid or gas, it is distributed via pipelines and has a calorific value of 141.9 kJ/g, which is 4.8 times greater than that of ethanol (29.7 kJ/g), 3 times greater than that of gasoline (47 kJ/g), and 2.6 times greater than that of natural gas (54 kJ/g) (Nanda et al, 2017).

Hydrogen, of the known elements, is the lightest and the most abundant in the universe, but it is naturally unavailable in its pure form and to be clean and sustainable it is essential to produce it cleanly and renewably. Although its production as energy vector has been long discussed, for now an affordable hydrogen generation and conversion technology has not been found. Currently, around 96% of hydrogen is generated from fossil fuels, with 29% from liquid hydrocarbons, 18% from coal, 4% from water electrolysis and 49% from natural gas (Abdin et al, 2020), where the methane steam reforming is the most comprehensive endothermic process for the generation of hydrogen-rich syngas. Natural gas is a kind of fossil fuel, and its usage fails to provide a solution to deal with the huge amount of carbon dioxide emissions during the reforming processes.

1.3. Mechanism and thermodynamics of SRE

The steam reforming of ethanol is a thermodynamically feasible, endothermic process with the following stoichiometry:

$$C_2H_5OH + 3H_2O \leftrightarrow 6H_2 + 2CO_2 \qquad \Delta H^\circ = 173.4\ \mathrm{kJ/mol} \tag{1}$$

To investigate how to maximize the yield of hydrogen and conversion of ethanol, it is important to understand the thermodynamics of the process. It has been widely shown in the literature that, from a thermodynamic point of view the steam reforming of ethanol is entirely feasible above 300 °C and produces H_2, CO_2, CH_4, CO and coke (Contreras et al, 2014).

Ethanol conversion and hydrogen selectivity depend on temperature, long term reaction, water/ethanol ratio, space velocity, contact time and presence of O_2. In order to reduce the concentration of by-products and increase the yield of hydrogen it was found that high temperature and high water to ethanol molar ratio (in the range 4-10) are favourable (Palma et al, 2012).

The reaction mechanism of the process is complex due to secondary reactions that take place in parallel to the steam reforming reaction and generate intermediate products and by-products, thus reducing H_2 yield. Example of side reactions that can take place (Montero et al, 2017) are:

Ethanol dehydrogenation	$C_2H_5OH \leftrightarrow C_2H_4O + H_2$	(2)
Ethanol dehydration	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	(3)
Ethanol decomposition	$2C_2H_5OH \rightarrow 3CH_4 + CO_2$	(4)
	$C_2H_5OH \rightarrow CH_4 + CO + H_2$	(5)
Acetic acid formation	$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2$	(6)
Acetone formation	$C_2H_5OH \rightarrow CH_3COCH_3 + CO + H_2$	(7)
Acetic acid steam reforming	$CH_3COOH + H_2O \rightarrow 2\ CO_2 + 4H_2$	(8)
Acetone steam reforming	$CH_3COCH_3 + 2H_2O \rightarrow 3CO + 5H_2$	(9)
Acetaldehyde decomposition	$C_2H_4O \rightarrow CH_4 + CO$	(10)
Acetaldehyde reforming	$C_2H_4O + H_2O \rightarrow 2CO + 3H_2$	(11)
	$C_2H_4O + 3H_2O \rightarrow 2CO_2 + 5H_2$	(12)
Incomplete ethanol reforming	$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$	(13)
Water gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	(14)
Methane steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	(15)
	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	(16)
Ethylene steam reforming.	$C_2H_4 + 2H_2O \rightarrow 4H_2 + 2CO$	(17)

Reactions that produce coke and contribute to catalyst deactivation are also present, such as:

Ethylene decomposition	$C_2H_4 \rightarrow 2C + 2H_2$	(18)
Boudouard reaction	$2CO \leftrightarrow C + CO_2$	(19)
Methane decomposition	$CH_4 \rightarrow 2H_2 + C$	(20)
Coke gasification	$C+H_2O \rightarrow CO + H_2$	(21)
Reverse of carbon gasification	$CO+H_2 \rightarrow C + H_2O$	(22)

The calculation of the thermodynamic equilibrium composition for the reaction and a steam to ethanol ratio of 3 reveals that hydrogen, CO, CO_2, and methane are the main products (Fig. 4) (Mattos et al, 2012). In runs without catalyst, a range of S/E of 3-9 and of temperature of 500-700°C, neither acetone nor acetic acid has been observed in the products (Montero et al, 2018).

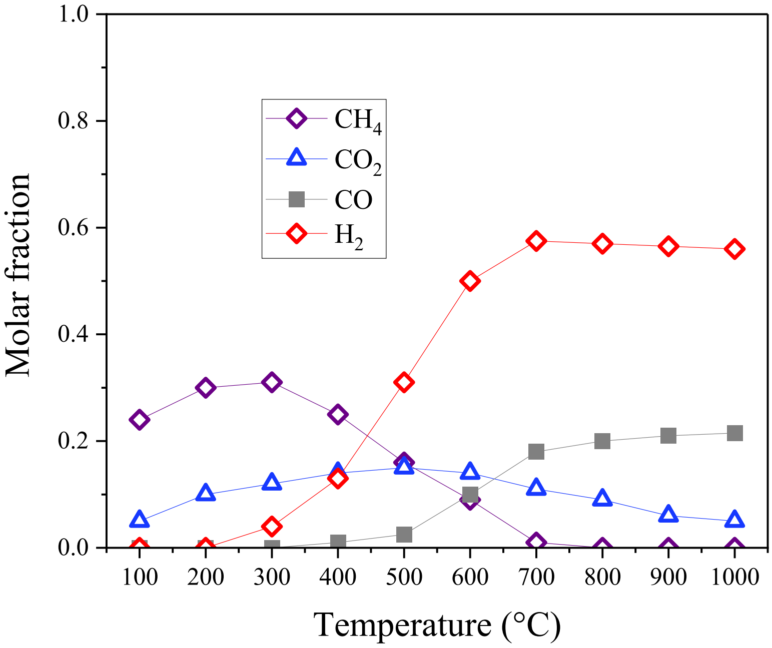

Figure 4: Molar fractions of steam reforming of ethanol products with temperature and a S/E=3 (Mattos et al, 2012)

At low temperatures, the cracking into CH_4 and CO_2 is thermodynamically favoured, (Palma et al, 2012) while at higher temperature it is the formation of H_2 and CO (Mattos et al, 2012). As the temperature is raised, methane and CO_2 concentrations decrease, whereas those of hydrogen and CO increase because WGS reaction and methane formation are favoured at lower temperatures. Moreover, increasing the reaction temperature leads to an increase in ethanol conversion, a decrease in the selectivities of acetaldehyde, acetone, and ethylene and an increase in those of H_2, CO, CO_2, and CH_4, as it can be seen in the product distribution versus reaction temperature in Fig. 4. Acetaldehyde, ethylene, and acetone are not predicted to be present at equilibrium because they are not thermodynamically stable products, but in practice, at low temperatures different undesirable byproducts are detected. This suggests that at low temperature reforming reactions are kinetically controlled and ethanol dehydrogenation (Eq 2) and dehydration (Eq 3) are faster than SRE. On the contrary, an increase in temperature seems to increase ethanol conversion and favours the steam reforming of ethanol and acetaldehyde. From the thermodynamic analysis of Palma et al, 2012, has been concluded that hydrogen production through bioethanol steam reforming is favoured at temperatures higher than 600°C, due to higher H_2 selectivity.

Although full conversion requires a molar ratio of steam/ethanol (S/E) = 3, a feed with excess water in the SRE shows advantages due to the role of water in the individual reactions of the kinetic scheme, as it favors H_2 selectivity and mitigates coke formation. At low water concentrations, from a thermodynamic point of view the reactions of ethanol decomposition are favoured (Fishtik et al, 2000) producing methane and CO_2 at lower temperatures and methane, CO and hydrogen at higher temperatures according to (Eq 4 and 5) respectively.

With an increase in the steam/ethanol molar ratio the steam reforming of ethanol (Eq 1) becomes the dominant reaction and also the water-gas-shift (Eq 14) and methane steam reforming reactions (Eq 15) increase. This leads to a reduction in the amount of the undesired products, such as CO and CH_4 and an increase in CO_2 and H_2.

In the study of Montero et al (2018), runs without catalyst at 500°C and a S/E in the range 3-9, have shown that ethanol conversion and hydrogen concentration are low and the results are not affected by the quantity of water in the feed. Above this temperature ethanol conversion and hydrogen yield rapidly increase. The trend of carbon products is different: acetaldehyde yield is high in 600-650° range, CO and CH4 yields increase above 650°C and CO_2 formation is almost insignificant in all the range studied.

1.4. Catalysts for SRE

Catalyst has been used in chemical industry for more than 100 years and nowadays the majority of processes in chemical engineer takes place with the use of a catalyst. Catalysis is the key to chemical transformations, where the catalyst accelerates a chemical reaction without affecting the position of the equilibrium (definition of Ostwald, 1895) and it can also influence the selectivity of chemical reactions. Also, regarding the steam reforming of ethanol, catalysts play a crucial role in terms of ethanol conversion, selectivity and hydrogen yield, and an understanding of the reaction pathways is fundamental for designing optimized catalyst.

In the literature the type of active phase and support has been widely investigated (Hou et al, 2015). Among active phase non-noble metals, mainly Ni, Co, and noble metals such as Rh, Ru, Pt, Pd and Ir have been taken in consideration. Regarding the support, if it exists, it can interact with ethanol and accelerates its transformation, thus influencing the catalyst activity. Not only it affects the reaction itself, but it can also provide highly active sites for reactions of C–C and C–H bonds and its choice can be critical for coke formation. Support materials include for example CeO_2, ZnO, MgO, Al_2O_3, zeolites-Y, TiO_2, SiO_2, $La_2O_2CO_3$, CeO_2-ZrO_2 and hydrotalcites (Contreras et al, 2014).

The selection of support played an important role in long-term catalyst operations. For example, γ- Al_2O_3, as acidic support, has been largely used because of its mechanical and thermal stability and a high specific surface area. Unfortunately, it induces ethanol dehydration to produce ethylene, which is a source of coke formation and that can show significant deactivation of catalysts after long-term operation. This side reaction can be depressed by adding K to neutralize the acidic support, or by using basic supports, as La_2O_3 and MgO.

When studying the reaction conditions of the process the type of catalyst has to be taken in consideration because the optimum temperature, H_2O-to-ethanol molar ratio and residence time range depend on the catalyst. Changes in catalytic activity and product selectivity are observed when changing these parameters.

One of the problems that has been encountered among the catalyst for this process is linked to catalyst deactivation, that can bring to loss of catalytic activity and/or selectivity over time. To avoid this phenomenon different strategies have been used, such as catalyst modification or change in operating conditions.

In literature, development of a highly active, stable and coke-resistant catalyst has been extensively undertaken. Different factors can determine the activity and stability of the catalyst as the nature of the metal, type of support, synthesis conditions, type of precursors, presence of additives and operating conditions.

As previously mentioned, the catalyst systems developed in the previous investigations can be generally classified into two categories, i.e., supported noble and non-noble metal catalysts (Hou et al, 2015). The general observation is that noble metals are normally more active and selective than transition metals, but they are also more expensive.

As noble metals active phase Rh, Ru, Pd and Pt have been widely investigated for the process and in Table 1 (Ni et al. 2007) is showed a comparison of the performances of alumina-supported noble metal catalysts for the process of ethanol reforming.

Based on conversion and selectivity Rh based catalysts present superior performance compared to the one of Pt, Pd, Ru, Au based catalysts. However, Rh is not very active for WGS reaction, which is important for CO removal in excessive presence of water.

Regarding the support CeO_2, MgO, and La_2O_3 are suitable for efficient ethanol reforming on Rh and high dispersion of catalyst atom at the support surface was found to enhance the activity of catalysts. The impregnation method, in terms of selectivity and conversion, produced the best noble catalyst (Contreras et al, 2014).

Also transition metals, especially Ni and Co with different percentages by weight and supports, have been widely studied for ethanol reforming, because of their lower cost as compared to noble metals. Some non-noble metal catalysts used in SRE are summarized in Table 2 (Ni et al. 2007), where Ni-based catalyst exhibited the best activity of ethanol conversion and selectivity to hydrogen.

Cobalt (Co) is a non-noble metal catalyst under extensive investigation as supported Co could break C–C bond. Al_2O_3 was reported to have the highest selectivity for steam reforming of ethanol by suppression of methanation and decomposition of ethanol. The selectivity of H_2 decreased in the order: Co/ Al_2O_3 > Co/ZrO2 > Co/MgO > Co/SiO_2 > Co/C.

Table 1. List of ethanol steam reforming using noble metal catalyst modified from Ni Meng et al. 2007

Catalyst	Support	Temperature (°C)	S/E	EtOH conversion	H_2 selectivity
Rh (1 wt%)	γ- Al_2O_3	800	3:1	100	~95
(2 wt%)				100	~96
Ru (1 wt%)				42	~55
(5 wt%)				100	~96
Pt (1 wt%)				60	~65
Pd (1 wt%)				55	~50
Rh (5 wt%)	γ-Al_2O_3		8.4:1	100% (at the beginning) 43% after 100h operation	Unknow
Rh (3 wt%)	MgO	650	8.5:1	99 (10h)	91
Pd (3 wt%)				10 (10 h)	70
Ni (21 wt%)				42 (10 h)	97
Co (21 wt%)				55 (10 h)	92
Ru (1 wt%)	CeO_2	450	Not known	Above 90 %	57 (20 min) 25 (100 min)
Rh (1 wt %)					82 (20 min) 56 (80 min)
Rh (2 wt%)	CeO_2	300	8:1	58.5	59.7
		400		100	66.3
		450		100	69.1
	ZrO_2	300		100	57.4
		450		100	70.3

Ni has high activity for C–C bond and O–H bond breaking and has high activity for hydrogenation, facilitating H atoms to form molecular H_2. However, Ni is less active for WGS reaction and suffers from coke formation and metal sintering at high temperatures, leading to considerable performance degradation during long-term operations. As it can be seen in Table 2, at 650 °C and with Ni loading of 10 wt%, almost 100% conversion of ethanol was attained for all catalysts.

For the Ni catalyst several supports and compounds have been studies as Al_2O_3, M-Al_2O_3 (M=La, Zr, Ti), Sn-La_2O_3, K-ZrO_2, $LiAlO_2$, $MgAl_2O_4$, Ce-$MgAl_2O_4$, SiO_2, Ce-SiO_2, zeolite (BEA and ZSM-5), mesoporous silica (SBA-15), Attapulgite ($(Mg,Al)_2Si_4O_{10}(OH)\cdot 4H_2O$), montmorillonite (MMT: $(Na,-Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2\cdot nH_2O$), CeO_2, $MCeO_2$ (M=La, Sm, Zr, Ca, Mg, K), graphene, Ni-containing perovskite oxides, Ni-Mg-Al hydrotalcite, and Ni-Mg-Al oxyhydride (Ogo et al, 2020). Elements such as La, Mg were added to increase the activity, W was added to Al_2O_3 to stabilize the catalyst. $NiAl_2O_4$ spinels were studied, obtaining conversion of 100% and selectivity to hydrogen of 70% (Contreras et al, 2014). For what it concerns the support, selectivity to hydrogen was found in the following decreasing order: $Ni/ZnO \approx Ni/La_2O_3 > Ni/MgO > Ni/\gamma\text{-}Al_2O_3$.

In the last years, Ni-based spinel-type oxides have been used as catalyst for the SRE. This type of catalyst has a high activity due to the fact that metal particles are highly dispersed by phase separation from the spinel oxide under a reducing atmosphere (Muroyama et al, 2010) and this can provide high performance for the reaction. The performance of this catalyst strongly depends on the components and crystallinity of the spinel-type oxides that affect the dispersion of nickel metal particles, and the residual supports under reducing condition. In particular, aluminate spinels generally present high thermal stability and melting points, mechanical stability, and resistance to alkalis and acids (Hasan et al, 2015).

In the study of Muroyama et al (2010) Ni-based spinel-type oxides, NiB_2O_4 (B= Al, Fe, Mn), synthesized by the citric acid complex method, were investigated for their catalysis of the ethanol steam reforming reaction. It was shown that in the range of temperature 250-550°C the initial conversion of ethanol was complete, and the products and catalytic stability depend on the B site metals. Among the B site metals studied $NiAl_2O_4$ catalyst exhibited stable ethanol conversion, H_2 yield and C_1 selectivity, showing to be a promising catalyst for ethanol steam reforming.

Table 2: List of ethanol steam reforming using non-noble metal catalyst modified from Ni et al., 2007.

Catalyst	Support	Temperature (°C)	S/E	EtOH conversion	H_2 selectivity
Ni (20 wt%)	La_2O_3	500	3:1	35	70
		800		~100	95
	γ-Al_2O_3	700		77	87
		800		100	96
Ni (20.6 wt%)	Y_2O_3	250	3:1	81.9	43.1
Ni (16.1 wt%)	γ- Al_2O_3			76	44
Ni (15.3 wt%)	La_2O_3			80.7	49.5
Ni (35 wt%)	γ- Al_2O_3	500	6:1	100	91
Ni (3.8 wt%)	Al_2O_3	450	3:1	96.6	61.5
		650		100	89
	Al_2O_3	450		100	0
		550		99.2	67.3
		650		100	87.4
Ni (10 wt%)	γ- Al_2O_3	650	8:1	100	78.2
	MgO			100	82.2
	La_2O_3			100	89.3
	ZnO			100	89.1
Co (10 wt%)	ZnO	350	4:1	100 (75 h)	73.4
Co (10 wt%), addition with Na					
Na (0.06 wt%)	ZnO	400	13:1	100	72.1
Na (0.23 wt%)				100	73.4
Na (0.78 wt%)				100	74.2
Co (8 wt%)	Al_2O_3	400	3:1	74	60-70
(18 wt%)				99	63-70
(8 wt%)	SiO_2			89	62-70
(18 wt%)				97	69-72

1.5. Effect of operating conditions

1.5.1. Temperature

Temperature has a noticeable effect on reaction pathways, conversion, selectivity, and catalyst stability. Runs without catalyst (using CSi as the only solid in the reactor) have proven that ethanol conversion is insignificant up to 500 °C (Vicente et al, 2014a), while the catalytic reaction can occur at lower temperature when using a catalyst, where optimum reaction temperatures depend on the type of catalyst that is used. On the one hand, the reaction is endothermic and so it is favored at high temperature, with higher conversion of ethanol and selectivity. Also, an increase in temperature prevents methane formation, considered one of the main by-product (Hou et al, 2015). On the other hand, at high temperature (>600°C) metal sintering can take place, energy demand is higher and the thermodynamic equilibrium of water-gas shift (WGS) reaction, which is important for increasing H_2 yield and lowering the CO concentration in the product stream, is disfavored. The occurring of WGS reaction increases with temperature until a certain value and then, due to thermodynamic, becomes disfavored.

The effect of temperature on catalyst performance has been largely investigated in the literature. Changes in catalytic activity and products selectivity occur at different ranges of temperature, depending on the nature of the catalyst, the S/E molar ratio and residence time. However, some behavior occurs frequently with different operating conditions and catalysts. At low reaction temperatures, a wide range of undesirable byproducts such as oxygenated compounds and hydrocarbons are detected (Mattos et al, 2012), suggesting that at low temperatures ethanol dehydrogenation and dehydration reactions are faster than the steam reforming reaction. With an increase in temperature ethanol conversion increases, with an increase in the selectivity of H_2, CO, CO_2, and CH_4. In fact, at higher temperatures the reforming reactions are more favorable.

This behavior was detected for example (Mattos et al, 2012), at temperatures lower than 200 °C K, for a La_2O_3-supported Ni catalyst (20 wt % of Ni), ethanol conversion was very low while at 350 °C was completed. Also, the final products detected were different with mostly acetaldehyde and hydrogen at 200 °C and an increase in of H_2, CO, CO_2, and CH_4 production at 350 °C, where acetaldehyde was no longer detected. At temperatures higher than 350 °C, in particular, the selectivity to H_2 and CO increased.

Also, for catalysts with a different acidity, as Ni/SiO_2 catalyst (Vicente et al. 2014a), an increase of temperature increases the ethanol conversion (complete at 500°C), the yield of H_2 and selectivity to H_2 (with a selectivity and yield of 0.8 at 700°C). Results showed that at a temperature of 300°C, the favoured reaction was ethanol decomposition dehydrogenation to C_2H_4O followed by decomposition of the latter to CH_4 and CO, and C_3H_6O formation. On the other hand, when the temperature was increased to 400°C WGS reactions and methanation acquired more importance. The increase in H_2 and CO_2 selectivity and the decrease in CO selectivity with higher temperature can be explained by the promotion of steam reforming and the WGS reactions. Increasing even more the temperature reaction leads to favor the steam reforming and dry reforming of methane, and disfavor WGS reaction (for temperature above 450°C) due to thermodynamic reasons.

1.5.2. S/E molar ratio

In the literature, the influence of the H_2O-to-ethanol molar ratio on the performance of different catalysts for SR of ethanol has been investigated, (Mattos et al. 2012) but in less detail than that of temperature. The SR of ethanol has been carried out using H_2O-to-ethanol molar ratios ranging from 1.0 to 15.0. In general, increasing the H_2O-to-ethanol molar ratio was found to increase the conversion of ethanol and H_2 production (Hou et al, 2015). With respect to product distribution, it was seen that, by increasing the amount of water in the feed, the production of H_2 and CO_2 also increased, and the rate of CO formation decreased. This indicates that the addition of water promotes the SR of ethanol and/or the WGS reaction. Furthermore, data indicate that increasing the H_2O-to-ethanol molar ratio also decrease the rates of formation of byproduct such as ethylene and acetaldehyde. The addition of water shifts the equilibrium of the dehydration reaction to favor the reactants and promotes the acetaldehyde decomposition reaction. However, the addition of large amounts of water implies higher operating costs for ethanol vaporization, which must be taken into account.

These results were shown for example by Montero et al. (2018), that studied the evolution of ethanol conversion and H_2 yield at 600 °C for a space time of 0.18 $g_{catalyst}/(g_{EtOH}/h)$ with a Ni/La_2O_3- αAl_2O_3 catalyst for a S/E molar ratio from 3 to 9.

Due to the high value of space time studied, ethanol conversion was full for all the S/E molar ratios studied, but a significant effect of this variable on H_2 yield was observed, as predicted by thermodynamics. Thus, H_2 yield increases almost linearly by increasing S/ E molar ratio, because the excess of water favours the reactions that produce H_2, such as ethanol and methane reforming, and WGS reaction. Concerning the selectivity of other products, as S/E ratio was increased, there was an almost linear increase in the selectivity of CO_2, whereas the selectivity to CO and CH_4 progressively decreases, as a consequence of the increase in the rates of WGS and CH_4 reforming reactions.

To complement the previous results, corresponding to total ethanol conversion, the effect of S/E molar ratio on ethanol conversion and H_2 yield was also studied with runs at low values of space time (0.04 $g_{catalyst}/(g_{EtOH}/h)$). Results showed that ethanol conversion in the 500–550 °C range (kinetic regime) was lower as the S/E molar ratio increased. This result evidences that an excess of water over the stoichiometric value attenuates the global reaction mechanism for ethanol steam reforming (Eqs. 1–17) due to the lower rate of some of the reactions in the kinetic scheme, such as ethanol dehydrogenation and dehydration, and ethanol and acetaldehyde decomposition. In the 500–550 °C temperature range, H_2 yield was slightly affected by an increase in the S/E molar ratio because the drop in ethanol conversion was balanced by the increase in H_2 selectivity.

Effect of steam/ethanol molar ratio was also studied for a $NiSO_2$ catalyst, with a space time of 0.053 $g_{catalyst}/(g_{EtOH}/h)$ and a temperature of 500°C (Vicente et al. 2014a) and results were coherent with those in the literature corresponding to different catalysts. Results showed that ethanol conversion and H_2 yield increased almost linearly with S/E ratio, and reached values of 0.98 and 0.49, respectively, for a S/E molar ratio of 10. CO_2 yield also increased, whereas those of CO and CH_4 decreased, suggesting that CH_4 reforming and WGS reaction were favoured and methanation reaction was disfavoured. A higher value of S/E molar ratio also increased CO_2/CO and $(CO_2 + CO)/ CH_4$ molar ratios, that confirmed that an excess of water in the reaction medium favours WGS reaction and attenuates methanation reaction, because water is a reactant in the former and a product in the latter. The decrease in H_2/CO_2 ratio (which tends to the stoichiometric value of 3) evidences that the excess of water favours the reforming reaction over ethanol decomposition. Regarding catalyst stability, under these conditions, steam/ethanol ratio seems not to have an important effect. This result is probably due to the fact that, for catalyst stability, the coke nature prevails over coke content. Over these conditions, best results were obtained with a S/E ratio of 6, considering H_2 production, energy cost and process scaling-up.

1.5.3. Space time

For catalytic reactions also the space time is a key factor that affects the conversion and the selectivity of the reaction. Space time is defined as the weight of catalyst divided by the flowrate of ethanol. In general, an increase in space time declines intermediates formation and enhances ethanol conversion and hydrogen selectivity (Hou et al, 2015).

Similar trends in the effect of space time in ethanol conversion and products yields have been observed in the literature for other Ni based catalysts, although the range of space time depends on catalyst composition and on the remaining reaction conditions.

For example, for the steam reforming of ethanol on Ni/La_2O_3-α Al_2O_3 catalyst (Montero et al. 2018), using S/E molar ratio in the range 3-9 and temperature of 500°C and 650°C, ethanol conversion increases in a pronounced way with space time, although more moderately at high temperatures due to the significant contribution of thermal routes to the reaction mechanism. In this case ethanol conversion increased with space time while the yield of hydrogen didn't have a monotone behaviour. In fact, the yield of hydrogen increased in a pronounced way with low value of space time (0.02–0.09 $g_{catalyst}/(g_{EtOH}/h)$ for all the temperature ranges studied until reaching a maximum at 0.09 $g_{catalyst}/(g_{EtOH}/h)$. Then when ethanol conversion was full, and temperature below 550 °C, H_2 yield decreased with an increase in space time and tended towards thermodynamic equilibrium values.

Also, for the reaction of steam reforming of ethanol on a Ni/SiO_2 catalyst (Vicente et al. 2014a) there are similar trends of ethanol conversion and products yields. Results showed that at 500 °C, ethanol partial pressure in the feed of 0.11 bar and a S/E=3 the ethanol conversion increases in a pronounced way with low value of space time and reaches a total conversion for 0.138 $g_{catalyst}/(g_{EtOH}/h)$, while the yield of hydrogen pass throws a relative maximum. Consistent with literature, after a certain value of space time the selectivity of H_2, CH_4, CO, CO_2 remained almost constant. In this case, based on results, it was showed that the increase in space time favors the contribution of WGS and methanation reactions to the global reaction mechanism and the reforming of acetaldehyde and acetone. Concerning catalyst deactivation, it was notably attenuated by increasing space time.

1.6. Problem of deactivation due to coke deposition or sintering

One of the main issues of catalytic steam reforming of ethanol is the stability of the catalyst, that has to be taken in account when designing the catalyst. In previews papers, four groups of catalyst deactivation mechanisms have been evidenced: coke formation, active metal sintering, active metal oxidation and poisoning (Hou et al, 2015).

Coke can destroy catalyst structure and occupy catalyst surface, thus it considerably reduces catalyst activity, causing a loss in hydrogen selectivity and ethanol conversion. In the literature (Vicente et al. 2014a) the origin of the deactivation by coke of the catalysts in the ESR reaction was attributed to the contribution of three main routes for coke formation: i) ethanol dehydration on the acid sites of the catalyst (Eq. 3) followed by polymerization of ethylene (Eq. 18); ii) Boudouard reaction (Eq. 19), and iii) methane decomposition (Eq.20). Carbon deposition appears to take place at the beginning of the reaction. The size of used catalyst particles increased with time on stream, as they were progressively enlarged by coke filaments, but the collisions between particles (favored by the mixing regime of the fluidized reactor) caused partial breakage of the coke on their surface. It was observed that coke content increased almost linearly with time on stream, and catalyst particle size also increased.

Another deactivation route of the catalyst is metal sintering (Vicente et al. 2014a), which can take place in transition metal catalysts when high temperatures (>600 °C for Ni) and high steam/ethanol molar ratios are used.

The extent of each deactivation cause (coke or sintering) depends on operation conditions (such as temperature and S/E ratio) and the catalyst used. Temperature plays an important role in carbon deposition because it affects the reaction pathway. At lower temperature, Boudouard reaction and hydrogenation of CO are the dominant reactions facilitating the carbon formation. Whereas, at high temperature Boudouard reaction reverses but carbon deposition facilitates through decomposition of hydrocarbons. Therefore, the intermediate reactions responsible for deposition of carbon are different at different temperatures (Sharma et al. 2017). At high temperature, water gas shift reaction leads to an increase in hydrogen productivity and a decrease in carbon deposition although it requires high energy consumption. The total amount of deposited carbon decreases as the reaction temperature increases. The same thing happens for water-to-ethanol molar ratio, for which an increase in S/E causes a decrease on coke produced. The concentration of water higher than stoichiometric quantity was reported to have an inhibitory effect on coke formation (Sharma et al, 2017). It has been studied that, in a wide range of temperature, a stoichiometric value of S/E molar ratio (3:1) is the minimum to avoid coke formation (Palma et al, 2012).

The acid/base properties of the support, which exhibits activity for this reaction, also determine the reaction pathways and, as a consequence, also influence catalyst stability (Mattos et al, 2012). Al_2O_3 support, that has been largely used thanks to its high surface area and stability, has an acidic site that promotes the formation of ethylene, that is a coke precursor. For what concerns Ni-based catalyst, basic oxide supports as La and Zr-based oxides have been used to suppress coke formation. Using CeO_2 based support prevent coke deposition due to its good oxygen storage capacity and oxygen mobility at its surface. Zeolite support can form small Ni particles, but their acidity causes carbon deposition. To improve catalyst stability, modifications of the support or Ni species have been studied. For example, adding Mg to Ni/Al_2O_3 catalyst delayed ethylene formation by neutralizing the acid sites of the support. The addition of K to Ni/MgO catalyst inhibits the sintering of Ni particles while its addition to Ni/Al_2O_3 reduces methane formation (Hou et al, 2015).

In literature, two types of coke with different effects on catalyst deactivation are distinguished: encapsulating coke and filamentous coke, as showed in the scheme in Fig. 5. The first one has amorphous nature and blocks metallic sites. It is associated with the polymerization of ethylene, and for this reason is favored by the presence of acid sites in the support. Instead, the filamentous one is structured in fibers and doesn't affect deactivation as much as the first one (Mattos et al, 2012). In fact, catalyst can remain active during the SR of ethanol despite having a considerable amount of carbon deposited behind the particles, because the filamentous particles cover the catalyst but do not hinder ethanol adsorption due to their porosity (Montero et al, 2015). The deactivating effect becomes important only when the filamentous coke blocks the access of the reactants to catalyst pores. The types of accumulated carbon depend on the nature of the active metal used and the reaction conditions (Hou et al, 2015). For noble metal-based catalyst, the carbon formed was the amorphous type, which encapsulated the active metal site and blocked the support surface. For transition metal (Ni, Co) catalyst, instead, filamentous carbon was usually observed.

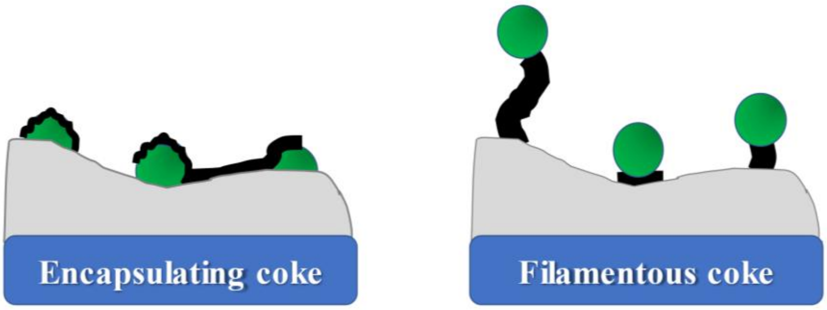

Figure 5: Scheme of types of coke

Characterization techniques revealed the formation of filamentous carbon in addition to amorphous carbon on Ni- or Co-based catalysts (Mattos et al, 2012). For example, the deactivation by coke deposition of Ni and Co catalysts in the steam reforming of ethanol has been studied in a fluidized bed reactor under the following conditions: 500 and 700 °C; steam/ethanol molar ratio, 6; space time 0.14 $g_{catalyst}/(g_{EtOH}/h)$, partial pressure of ethanol in the feed 0.11 bar, and time on stream up to 20 h (Vicente et al. 2014b). At 500 °C (suitable temperature for enhancing the WGS reaction, decreasing energy requirements and avoiding Ni sintering), both encapsulating and filamentous coke was present. The main cause of deactivation was linked to the encapsulating coke fraction (monoatomic and polymeric carbon) that blocks metallic sites, whereas the fibrous coke fraction (filamentous carbon) coats catalyst particles and increases their size with time on stream with a low effect on deactivation, especially for catalysts with high surface area. Coke deposition was drastically attenuated at 700 °C, temperature at which coke gasification is very rapid, and the remaining coke is highly condensed (high C/H ratio). Nevertheless, metal site sintering occurs at this temperature, with a noticeable increase in metal crystal size. Coke deposition has been generally considered as a negative factor in the design of the catalyst, but the formation of certain type of carbon on Ni surface can be positive, increasing stability and activity of the catalyst. Many researchers have found out that filamentous carbons formed during steam reforming process, using a Ni-based catalyst, is in the shape of carbon nanotubes (CNTs) (Quan et al, 2019). This material has attracted considerable attentions worldwide because of its particular physical and chemical properties and has a number of applications that have prospects in application to biomedicine, catalysis, electronics, and hydrogen storage. Substantial economic worth to produce H_2 via catalytic steam reforming of ethanol could be added by the highly valued CNTs as for Ni catalyst supported on SiO_2 fiber (Ogo et al, 2020). In the study of Quan et al (2019) for a 10% Ni/CaO catalyst, used in the steam reforming of ethanol, TEM images demonstrated that the CNTs were the main carbon products accompanied with some amorphous carbons.

1.7. Objectives

This work has the scope of analysing a Ni-Al_2O_4 derived spinel catalyst for the catalysis of the ethanol steam reforming reaction. The reaction has been studied in the literature over Ni-based spinel-type oxides without reduction treatment and, through these studies, it was confirmed that nickel-based spinel-type oxides are promising catalysts for ethanol steam reforming. In fact, these studies point out that Ni-based spinel-type oxides catalyst exhibited stable ethanol conversion, H_2 yield and C_1 selectivity, and the structure of $NiAl_2O_4$ was stable due to its low reducibility. (Muroyama et al, 2010; Nuñez Meireles et al, 2019).

These Ni-based spinel-type oxides catalysts, however, were not reduced before the reaction, so this study attempts to understand the behaviour of the reduced catalyst in a large range of operation conditions, in order to understand the reaction pathway of the process and the optimum conditions. Moreover, the study also focuses on coke deposition, the reaction pathways that lead to it, how it influences the deactivation of the catalyst and the morphology of the coke that was formed.

2. EXPERIMENTAL

The experimental part has been carried out at the Laboratories of the Chemical Engineering Department in the Faculty of Science and Technology (in Leioa) of the University of the Basque Country (UPV-EHU). The aim of the study was to understand how operating conditions affected the steam reforming reaction using a $NiAl_2O_4$ spinel derived catalyst in order to find the optimum values of temperature, space time and S/E molar ratio.

2.1. Catalyst preparation and characterization

The $NiAl_2O_4$ catalyst was prepared by the co-precipitation method, used by Arandia et al, (2020). The process lasted approximately 8 hours and was conducted by the drop-by-drop addition under constant stirring of ammonium hydroxide as precipitating agent (NH_4OH 0.6 M) into an aqueous solution of a mixture of $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_2 \cdot 9H_2O$, until a ph of 8 was reached. Then the mixture was filtered with two filters, one made of paper and one of 0.8 µm, and washed with water.

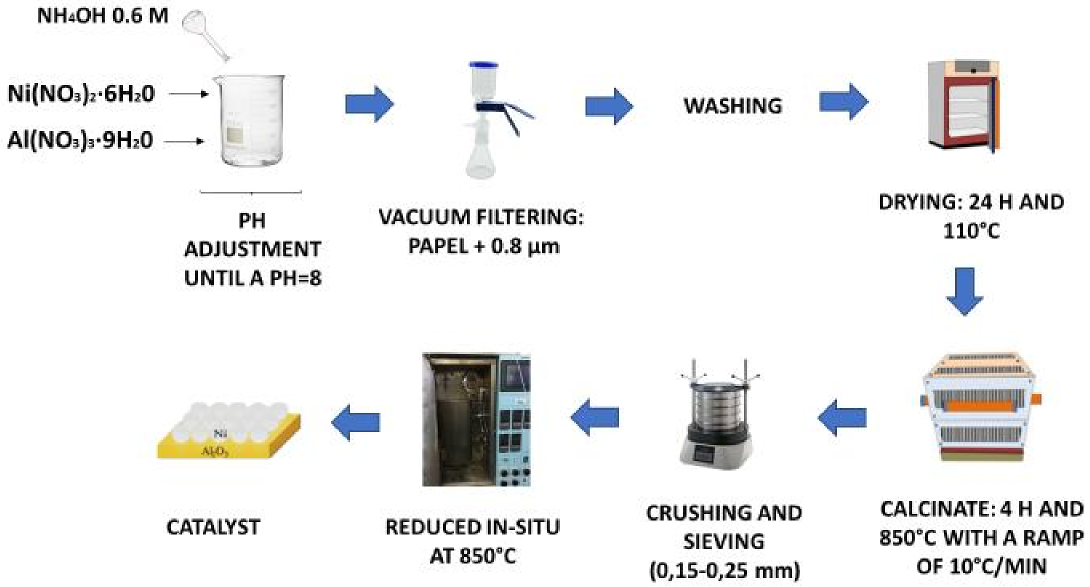

Figure 6: Catalyst preparation scheme

The filtered part was put in an oven for 24 h at 110°C and then calcinated at 850°C for 4 h with a heating ramp of 10°C/min. Once it was calcined, it was grounded in order to obtain particle size of 0.15-0.25 mm. The size of Ni particle influences the reaction. In fact, an increase in Ni active particle size to 25-30 nm, shows a lower H_2 yield and promotes the formation of coke. The amount of Ni and Al nitrate salt precursors are those corresponding to 33 wt% of Ni (stoichiometric value for the $NiAl_2O_4$ spinel).

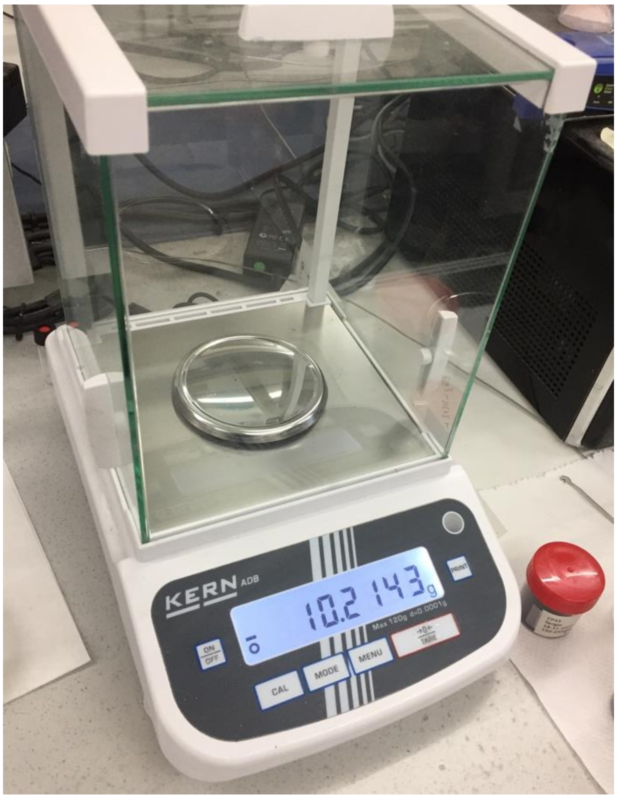

Figure 7: Photo of the scale used to weight the catalyst

Prior to the kinetic runs, the catalyst was reduced in situ by using a hydrogen flow of 10 ml/min and a nitrogen flow of 135 ml/min at 850° C with a ramp of 10°C/min. These conditions were selected on the base of TPR profile, showed in Fig. 8. These conditions assured complete reduction of $NiAl_2O_4$ spinel so that Ni^0 particles were well dispersed on the Al_2O_3 support.

Temperature programmed reduction (TPR) measurements were conducted on an AutoChem II 2920 Micromeritics. The TPR profile of $NiAl_2O_4$ spinel indicates that the maximum H_2 uptake takes place at 760 ºC, corresponding to the reduction of Ni species, which confirms that Ni is mostly incorporated in the spinel structure, which corresponds to the reduction of the $NiAl_2O_4$ spinel phase (Remiro et al., 2018).

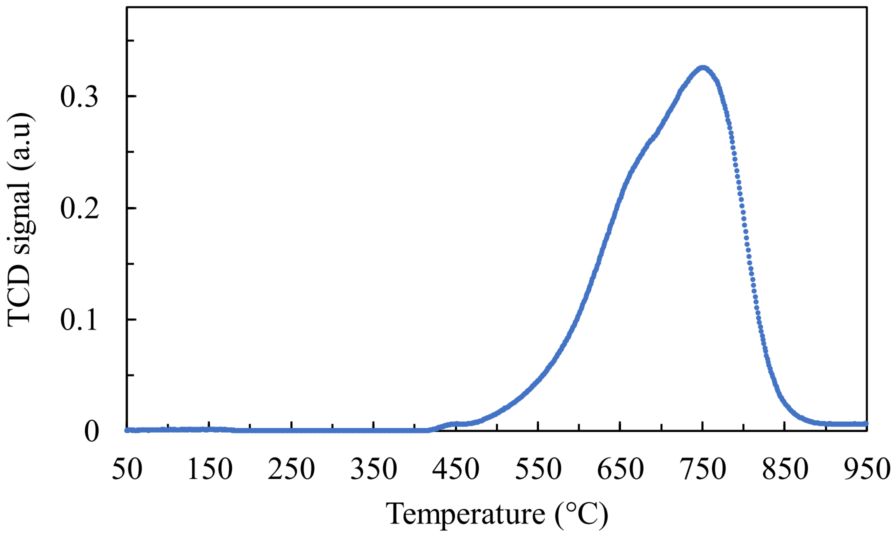

Figure 8: TPR profile

The identification of crystalline phases and the morphological study was carried out by X-ray diffraction conducted on a Bruker D8 Advance diffractometer with $CuK_{\alpha 1}$ wavelength of 1.5418 Å. Fig. 9 a and b show the X-ray diffraction (XRD) for oxidized and reduced catalyst, respectively.

The XRD pattern oxidized catalyst (Figure 9a) indicates the formation of the typical cubic structure expected for this spinel, showing peaks at $2\theta = 31.2$, 37, 45.1, 59.7 and 65.6°. Diffraction lines corresponding to segregated phases of Al_2O_3 were not detected. Upon reducing the $NiAl_2O_4$ spinel structure, the XRD pattern of reduced catalyst (Figure 9b) shows peaks at $2\theta = 44.65$ and 51.95° corresponding to reduced Ni crystals and at $2\theta = 37$, 44.65 and 67.14° corresponding to Al_2O_3 phases. This indicates that the reduction process at 850 °C completely converted $NiAl_2O_4$ spinel into reduced Ni crystals supported on Al_2O_3 (Ni/Al_2O_3), as previously reported in other works. We used the Scherrer equation (Eq. 23) to estimate the mean reduced Ni crystal size using the diffraction peak at $2\theta = 51.95°$ and obtained a mean size of 26 nm for the batch of $NiAl_2O_4$ spinel reduced in the reactor. This large size of Ni crystal is probably due to the fact that a large amount of catalyst mass was reduced and the sintering of the metal particles occurred, due to the temperature. That large size of Ni crystals is probably responsible for the large amount of carbon nanotubes that are formed with this catalyst.

Scherrer equation:
$$\tau = \frac{K\,\lambda}{\beta\, cos\theta} \tag{23}$$

Where τ is the average crystallite size, K is a dimensionless shape factor (K=0.9), λ is the X-ray wavelength ($\lambda = 1.541874$), β is the line broadening in radians and θ is the Bragg angle.

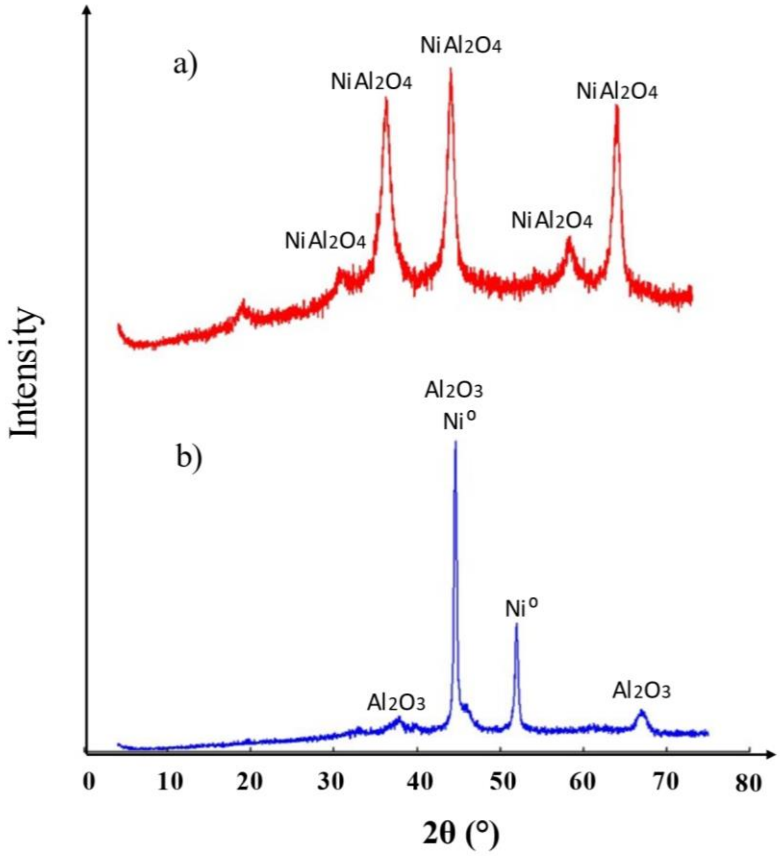

Figure 9: XRD of oxidized (a) and reduced (b) catalyst.

2.2 Reaction equipment

The kinetic runs have been carried out in automated reaction equipment (Microactivity Reference from PID Eng & Tech) provided with an isothermal fluidized bed reactor (22 mm of internal diameter and total length of 460 mm) (Fig. 10) connected on-line to a gas chromatograph (Agilent Micro-GC 3000) for product analysis. The catalyst was mixed with an inert solid (CSi, particle size of 105 µm) because it was showed in previous works that it provides a good fluidization regime and decreases the minimum fluidization velocity required for the catalyst alone. As showed in literature (Montero et al, 2018), the use of the fluidized bed is a good choice because it guarantees a good control of the temperature and attenuates the deactivation of the catalyst due to coke deposition. The feed was a gas mixture of ethanol, water, nitrogen. A small portion of the effluent stream of the second unit (fluidized-bed reactor) is diluted in an He stream and sent continuously through a thermally insulated line (at 150 ºC) to a micro gas chromatograph (MicroGC 490 Agilent) for the on-line analysis of its composition. The flowrate was adjusted in order to have in the feed an ethanol molar composition of 5% and the desired S/E ratio.

The Micro-GC is provided with four modules for the analysis of: 1) permanent gases; 2) oxygenates, light olefins (C2-C3) and water; 3) C2-C6 hydrocarbons; 4) C6-C12 hydrocarbons and oxygenate compounds. The compounds were quantified and identified using calibration standards of known concentration.

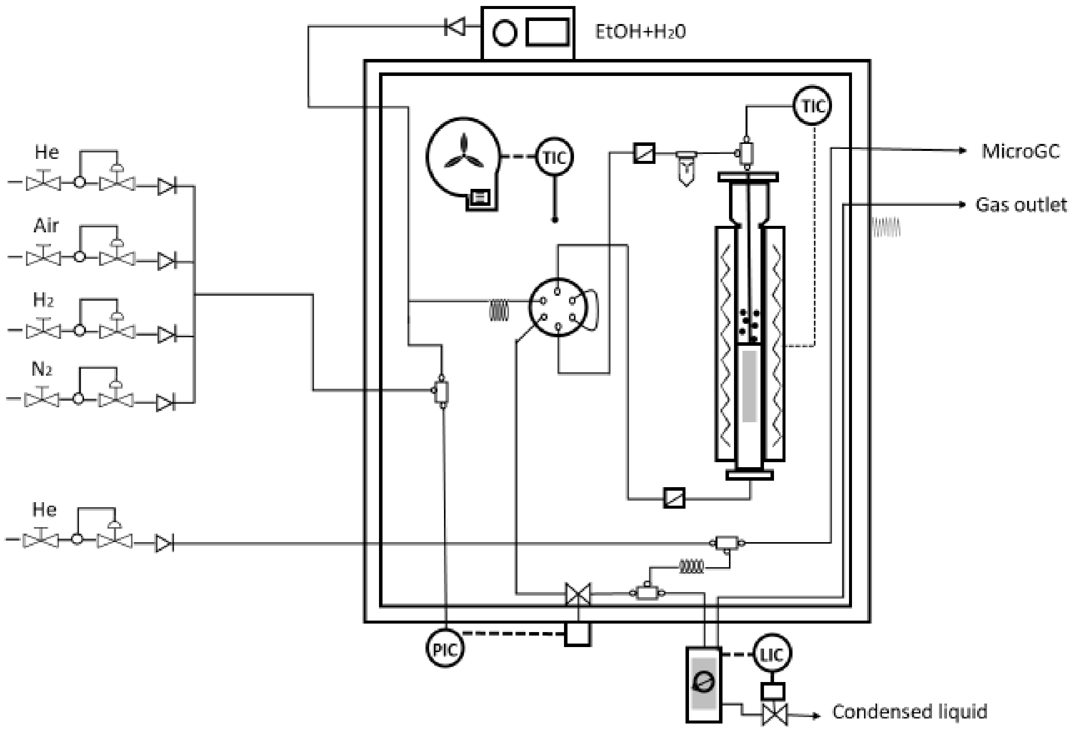

Figure 10: Scheme of reaction equipment

Figure 11: Photo of reaction equipment

Figure 12: Photo of the reactor used

The catalyst performance has been studied for different operating conditions of temperature, steam/ethanol molar ratio and space time and a total pressure of 1.7 bar. The temperature range was between 450 and 650°C but the reaction was mostly studied for temperatures of 500 and 600°C. The studied S/E ratio was 3, 6 and 9 and the space time range was between 0.0075 and 0.2 $g_{catalyst}/(g_{EtOH}/h)$.

In order to compare the kinetic behaviors of the catalyst in the different operating conditions, the ethanol conversion, the yield of products have been calculated for each reaction.

The ethanol conversion was calculated as:

$$X_{Eth} = \frac{F_{E0} - F_E}{F_{E0}}$$

where F_{E0} and F_E are the ethanol molar flow rates at the reactor inlet and outlet, respectively.

The products yield is calculated as:

$$Y_i = \frac{F_i}{\nu\, F_{E0}}$$

Where F_i is the molar flow rate of product i and $\nu\, F_{E0}$ is the maximum flow rate that may be obtained according to stoichiometry when ethanol is fed into the reactor. ν is the stoichiometric coefficient between product i and ethanol, whose value is 6 for the hydrogen, 2 for the CO_2, CO, CH_4 and 1 for C_2H_4, C_2H_4O and C_2H_6.

At the end the moles of C in the inlet and in the outlet have been calculated in order to evaluate the quantity of carbon that was not present in the gaseous outlet stream and so it was transformed to solid carbon deposits (coke).

To study the quantity of coke that was deposited in the catalyst during the reaction, at the end of each reaction the catalyst was weighted. The amount of carbon deposited on the catalyst was calculated, by subtracting the initial weight of the catalyst from the final one, that accounts for the mass of the catalysts plus de carbon deposited.

This measurement of the carbon content deposited on the catalyst provides a more reliable value in respect to the usual method where the weight loss in programmed temperature oxidation analysis (TPO) is calculated and it is useful to understand how operating conditions influence coke deposition. In the analysis of the coke content by TPO analysis a correct homogenisation of the deactivated catalyst bed is needed in order to have a representative sample for the analysis. Vicente et al. (2014b) found out that the bed of deactivated catalyst in the SRE may contain particles of very different sizes (due to uneven growth of carbon nanotubes deposited on the different catalyst particles), and the coke content analysed by TPO varied significantly according to the size of the particles analysed.

3. RESULTS

3.1. Effect of operating conditions on reaction indices for fresh catalyst

3.1.1. Temperature

Regarding temperature, we want the best performance (higher yield of hydrogen, higher conversion of ethanol and no deactivation) using the lowest possible temperature, to have low heating cost.

The effect that temperature has on the reaction indices is shown in Figs. 13 and 14, in which the values are shown for ethanol conversion and H_2 yield (Fig. 13), and carbon products yields (Fig. 14), with a S/E=3 and a value of space time in kinetic regime (0.025 $g_{catalyst}/(g_{EtOH}/h)$).

As it can be observed, the yield of hydrogen and the conversion of ethanol increase with the increasing of temperature, that is consistent with the literature (Vicente et al. 2014a). At 450°C the conversion of ethanol is already high (0.8), and after 500 °C is almost complete.

In the 500-600 °C range of temperature there is an increase in the yield of CO_2, C_2H_4 and CO, whereas the yield of methane decreases. The same trend in conversion and yield with temperature occurs for higher value of space time, in thermodynamic regime, (as it will be seen in section 3.1.3). This is probably because an increase in temperature in this range favors ethanol dehydration (Eq. 3), WGS reaction (Eq. 13) and methane steam reforming (Eq. 15 and 16). In particular, methane yield decreases almost linearly with temperature and a CO yield increases at the same time, showing that at high temperatures the methane steam reforming reaction (Eq. 15), that is a highly endothermic reaction, has an important contribution in the overall scheme reactions, also leading to a higher hydrogen yield.

The yield of C_2H_4 has a consistent increase with an increase in temperature, and that could be explained by assuming that the ethanol dehydration becomes more important than SRE reaction. However, as it will be shown later in section 3.2, when analyzing the evolution of reaction rates over time, this is not the case, since at 4 h reaction time (catalyst partially deactivated) C_2H_4 yield decreases as the temperature increases, indicating that the ethanol SR reaction is favored over the dehydration of ethanol at high temperature. Therefore, this increase in ethylene yield at the onset of the reaction should be attributed to the fact that ethylene is a primary reaction product (as clearly shown in section 3.1.3) and the reaction of ethylene conversion by decomposition (to H_2 and carbon) is disfavored with an increase in temperature.

The quantity of acetaldehyde produced using this catalyst is low in 450-600°C temperature range, showing that for these temperatures ethanol dehydrogenation occurs to a low extent, being slightly more important at high temperature.

For higher temperature (650°C) the yield in CO_2 and H_2 decreases while the ones of CO, C_2H_4 and acetaldehyde increase. At this temperature reaction pathway is different and ethylene yield is high, showing that ethylene decomposition to hydrogen and carbon is disfavored and, for this reason, hydrogen yield is lower. At this temperature ethanol dehydrogenation (Eq 2) and dehydration (Eq 3) are favoured so acetaldehyde can be found in the products.

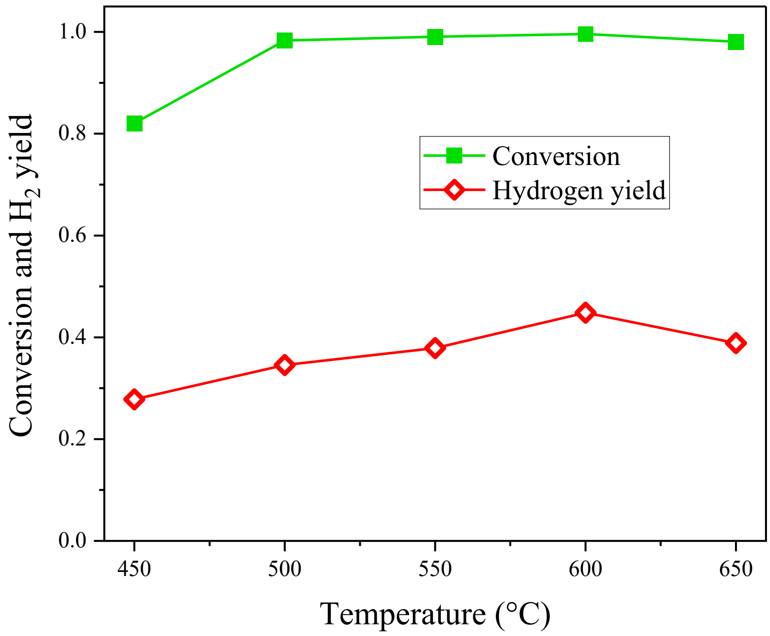

Figure 13: Conversion of ethanol and hydrogen yield at different temperature with a S/E=3 and a space time of 0.025 $g_{catalyst}/(g_{EtOH}/h)$

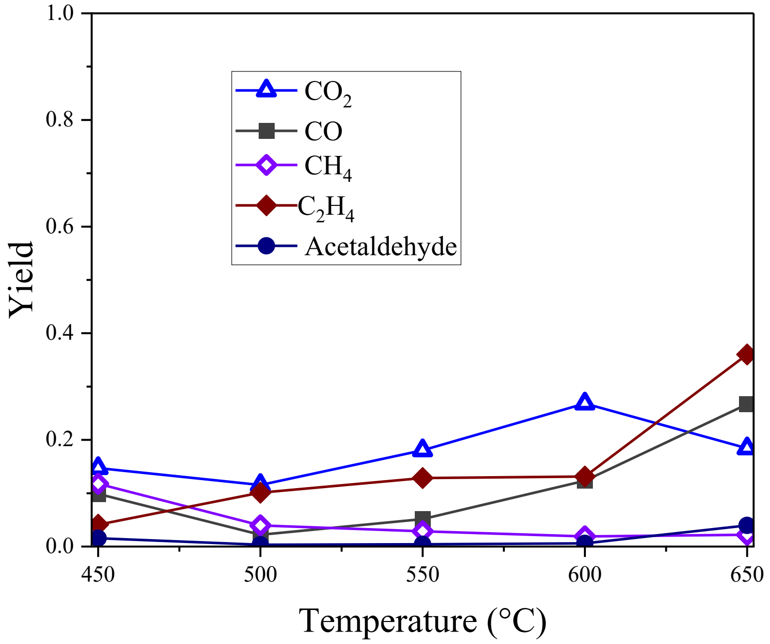

Figure 14: Yield of products at different values of temperature with a S/E=3 and a space time of 0.025 $g_{catalyst}/(g_{EtOH}/h)$.

3.1.2 S/E molar ratio

Regarding the effect of S/E ratio, in literature it is pointed out that, for high value of space time, conversion and hydrogen yield increase when a larger quantity of water is used.

However, the quantity of water in the feed affects the reactions in different-ways for different value of space time, so the behavior should be studied for both kinetic and thermodynamic regime.

For high value of space time, as it can be seen in Fig 15, for a temperature of 600°C and a space time of 0.1 $g_{catalyst}/(g_{EtOH}/h)$ (thermodynamic regime) the hydrogen yield increases and we have a total conversion.

In Fig 16, the yields of carbonaceous products for the same operating conditions are shown. With excess of water, CH_4 reforming and WGS reaction are favoured while methanation reaction is disfavoured and for these reasons CO_2 and H2 yields increase almost linearly, whereas those of CO and CH_4 decrease. The yields of acetaldehyde and ethylene have not been plotted in Fig. 16 because their presence has not been detected for this high value of space time.

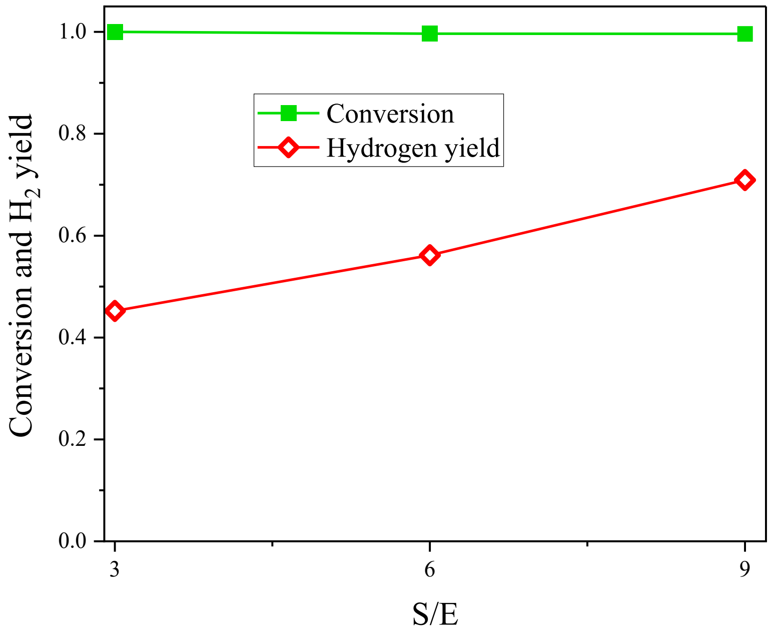

Figure 15: Ethanol conversions and hydrogen yield as a function of S/E molar ratio, T=600°C and 0.1 $g_{catalyst}/(g_{EtOH}/h)$.

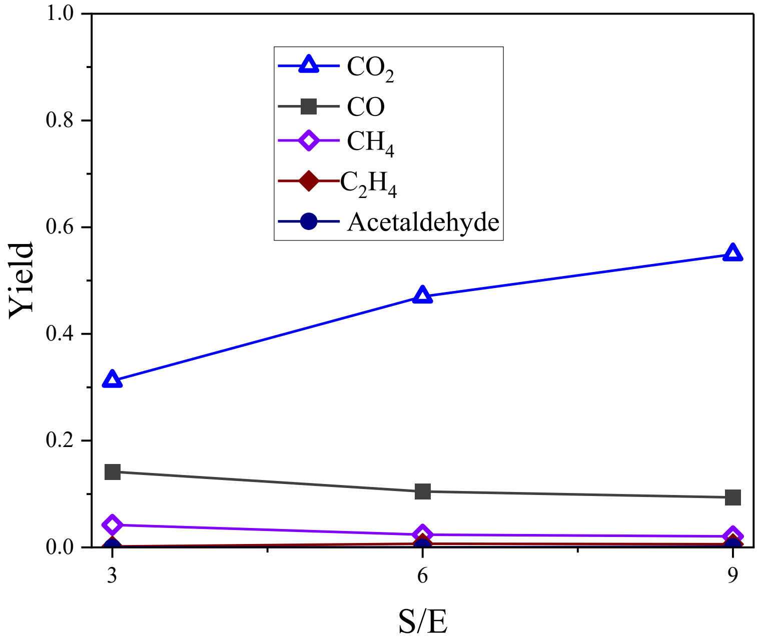

Figure 16: Yield of products as a function of S/E molar ratio, T=600°C and 0.1 $g_{catalyst}/(g_{EtOH}/h)$.

For low value of space time, as it can be seen in Fig. 17, for a temperature of 600°C and a space time of 0.01 $g_{catalyst}/(g_{EtOH}/h)$ (kinetic regime) the hydrogen yield remains almost constant with S/E molar ratio, while the conversion is lower for higher quantity of water in the feed. This trend in conversion is due to the fact that water inhibited the overall mechanism reaction when in kinetic regime.

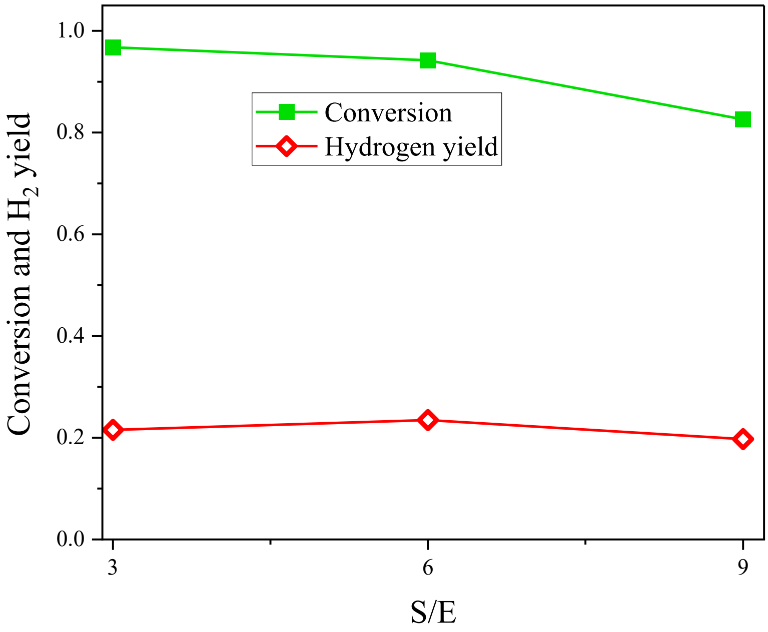

Figure 17: Ethanol conversion and hydrogen yield as a function of S/E molar ratio, T=600°C and 0.01 $g_{catalyst}/(g_{EtOH}/h)$.

In Fig. 18, the yields of carbonaceous products for the same operating conditions are shown. Increasing the S/E molar ratio seems not to affect the reaction pathway in this case, with products yield that remains constant in the S/E range. With this low value of space time the yield in ethylene is high, showing that ethanol dehydration occurs but then ethylene decomposition is not favoured.

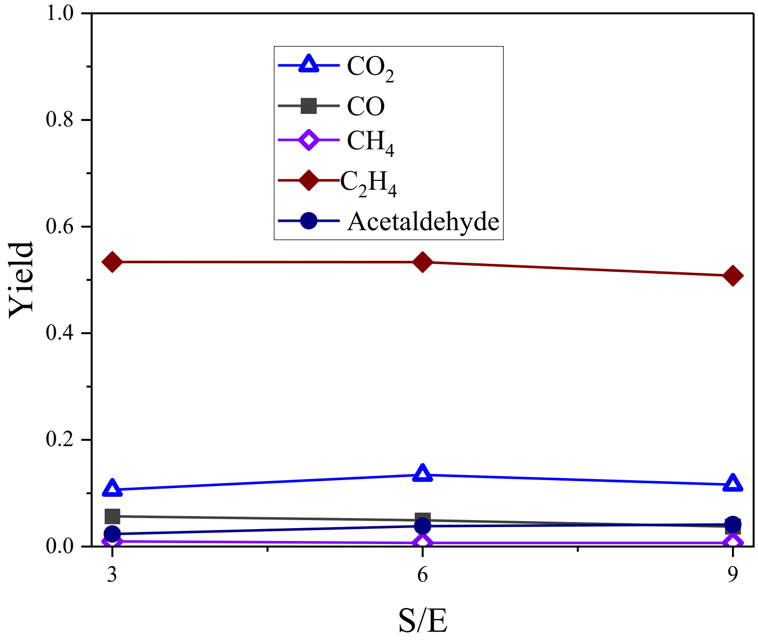

Figure 18: Yield of products as a function of S/E molar ratio, T=600°C and 0.01 $g_{catalyst}/(g_{EtOH}/h)$.

3.1.3 Space time

Another parameter that influences the performance of the process is the space time, defined as the weight of catalyst divided by the flowrate of ethanol.

In Fig. 19 the yield of hydrogen and the conversion of ethanol at temperatures of 500°C and 600°C and a S/E=3 are represented. As we can notice, the yield of hydrogen for a temperature of 500 °C increases with the increase of space time and the rate of increase is higher when the space time is less than 0.05 $g_{catalyst}/(g_{EtOH}/h)$). Conversion is complete at 0.05 $g_{catalyst}/(g_{EtOH}/h)$ at 500°C and at 0.025 $g_{catalyst}/(g_{EtOH}/h)$ at 600°C.

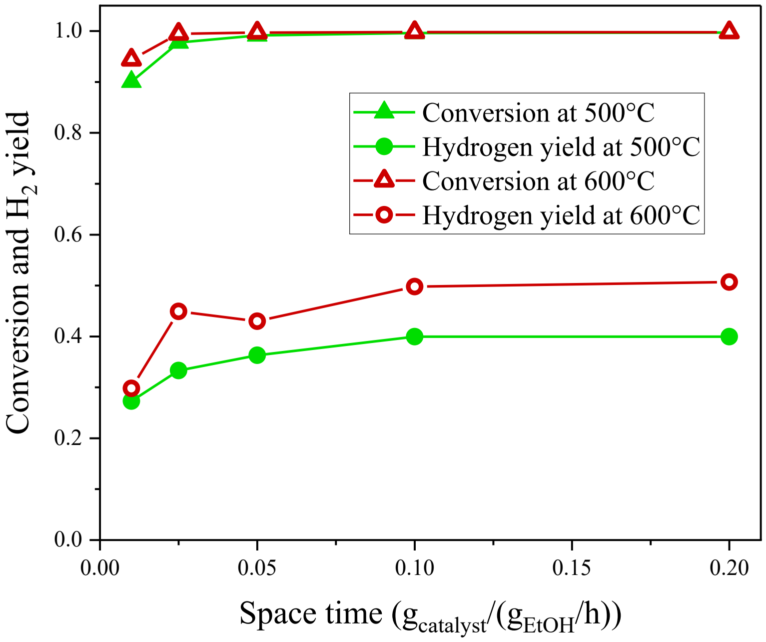

Figure 19: Ethanol conversion (Δ) and hydrogen yield (●) as a function of space time at 500°C and 600°C and a S/E=3

In Fig. 20 and 21 the yield of carbonaceous products at a S/E=3 and temperatures of 500°C and 600°C respectively are represented. As it can be noticed, for low values of space time the yield of ethylene is high and then it decreases. This is because ethylene is an intermediate that is rapidly formed by ethanol dehydration (Eq 3) and then rapidly decompose to hydrogen and carbon at higher values of space time.

Acetaldehyde is detected only for lowest value of space time, showing that it is formed during the reaction but as an intermediate, that rapidly reacts to probably give CO_2.

On the contrary, the yield of CO_2, CH_4, CO and H_2 increases. This is because with higher values of space time the rates of intermediate reactions are faster, and they rapidly convert to final products.

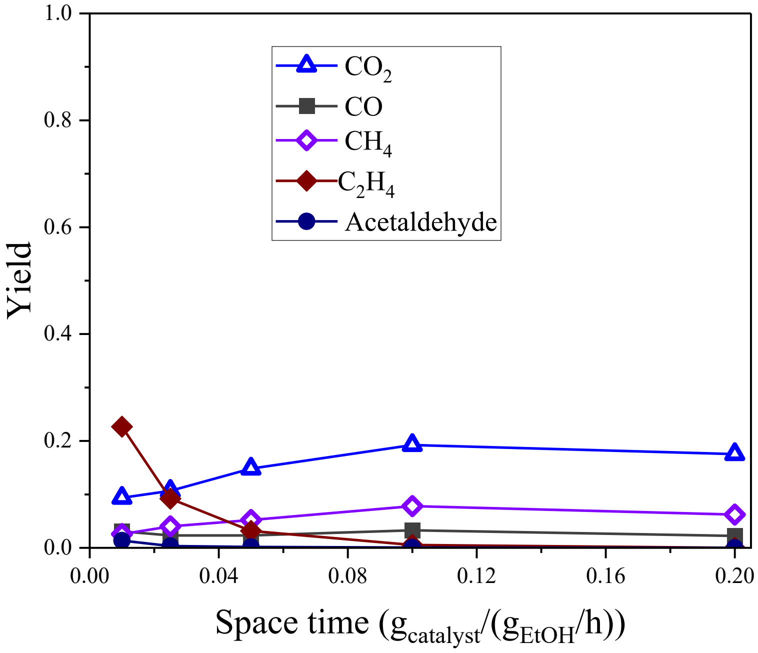

Figure 20: Yield of carbon products as a function of space time at T=500°C and a S/E=3

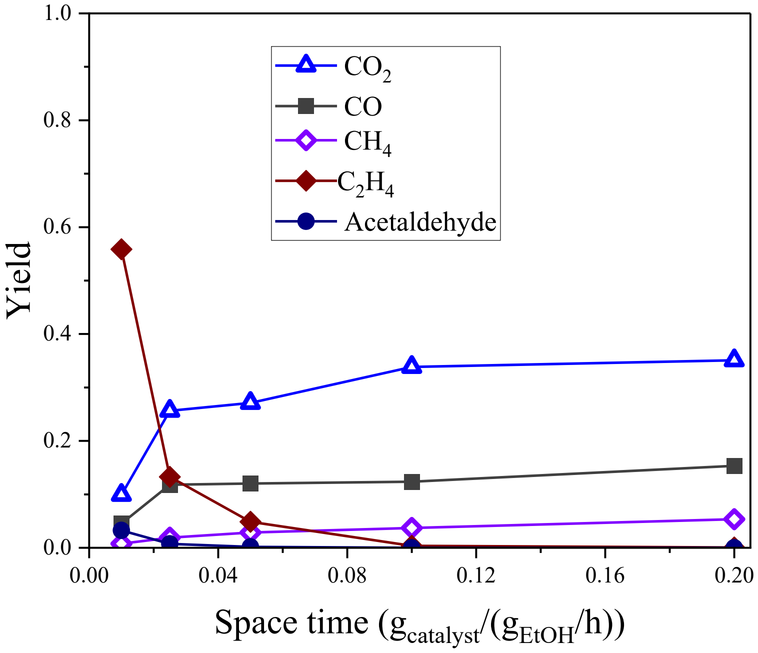

Figure 21: Yields of carbon product as a function of space time at T=600°C and a S/E=3

3.2. Effect of operating conditions on the evolution of reaction indices with time on stream

3.2.1 Temperature

Temperature does not only affect the reaction pathway but also the stability of the catalyst with time on stream. Figs. 22 and 23 show the evolution of the reaction indices with time on stream for 0.025 $g_{catalyst}/(g_{EtOH}/h)$ (low space time) and temperature of 500°C and 600 °C respectively. For both temperatures the yield in hydrogen decreases with time on stream at the same time ethylene yield increases. This is because at the beginning ethylene is formed but it is present only as an intermediate, quickly decomposing to hydrogen and carbon on the active sites of alumina. However, ethylene decomposition reaction is quickly deactivated at this low value of space time while its formation through ethanol dehydration is not deactivated.

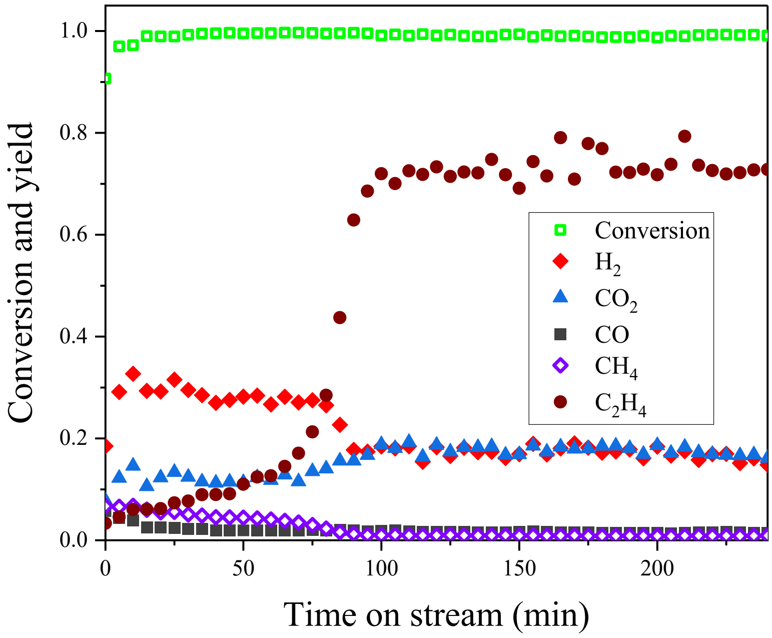

Figure 22: Ethanol conversion and products yield with time on stream at 500°C, S/E=3, 0.025 $g_{catalyst}/(g_{EtOH}/h)$.

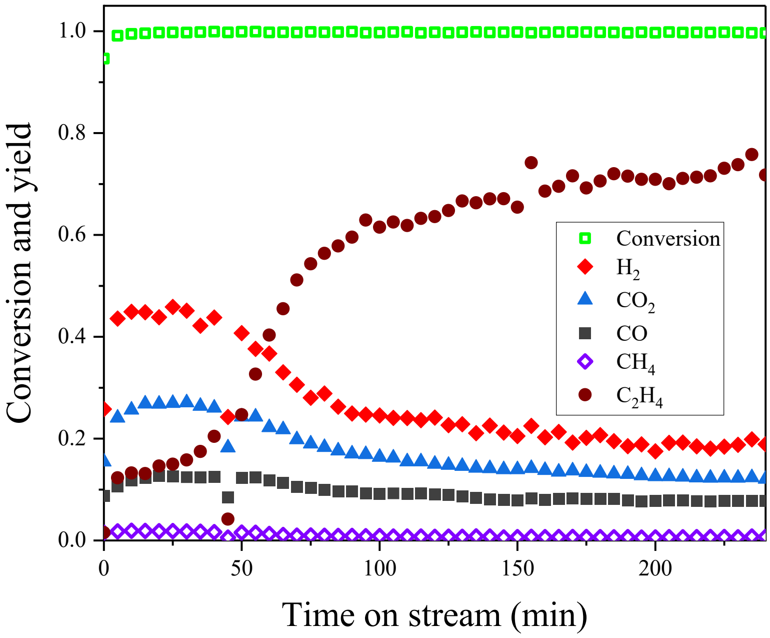

Figure 23: Ethanol conversion and products yield with time on stream at 600°C, S/E=3, 0.025 $g_{catalyst}/(g_{EtOH}/h)$.

At lower temperature the deactivation of ethylene decomposition occurs after a higher time on stream. This is probably because at higher temperature this reaction is faster and carbon is formed more rapidly, and the deactivation of this reaction is more rapid too.

For temperature higher than 600°C conversion decreases with time on stream. This can be seen from the time on stream for a temperature of 650°C, in Fig. 24. It is possible that at high temperature, at the beginning of the reaction a different type of coke is formed, and this coke leads to a more severe catalyst deactivation. The acetaldehyde formed by ethanol dehydrogenation, which is a significant reaction route at high temperature, would be responsible of the formation of an amorphous and encapsulating coke, that causes a rapid deactivation for the reactions occurring both on metal sites and also on the acid sites of the Al_2O_3 support (Montero et al., 2018). With this rapid deactivation of the catalyst, the ethylene that is formed does not react to form hydrogen and solid carbon. Moreover, this type of amorphous carbon causes a significant deactivation of the ethanol dehydration reaction, which explain the decrease in the yield of ethylene along time on stream.

Temperature reaction also affects the quantity of coke that is deposited on the catalyst (Fig. 25).

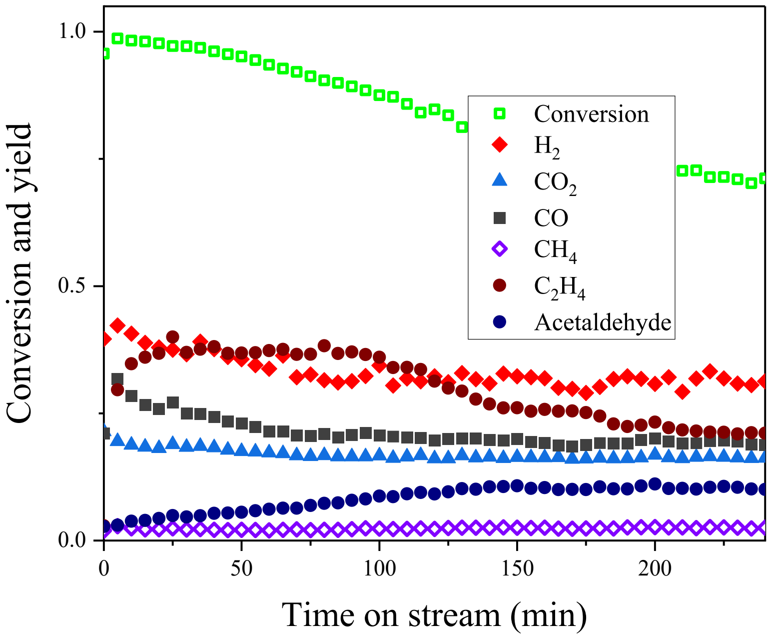

Figure 24: Ethanol conversion and products yield with time on stream at 650°C, S/E=3, 0.025 $g_{catalyst}/(g_{EtOH}/h)$.

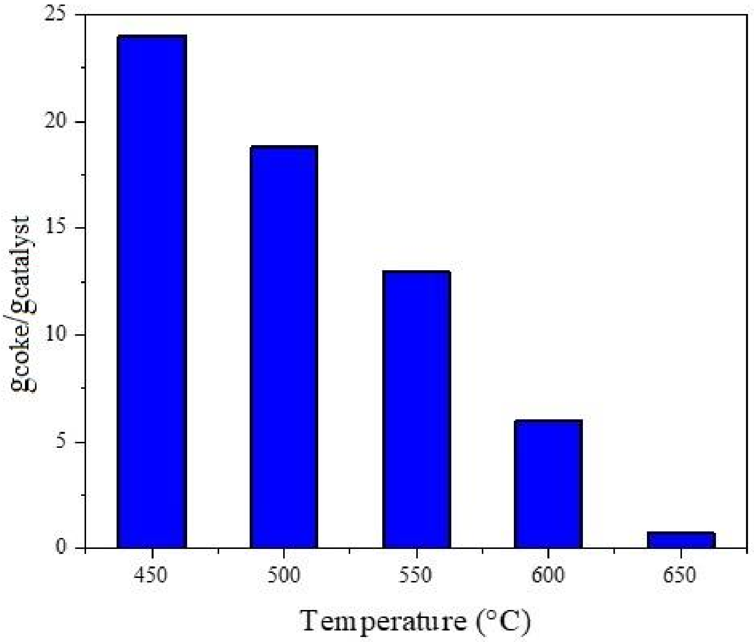

Figure 25: Quantity of coke per gram of catalyst after 4 hours reaction for different temperatures, S/E=3 and 0.025 $g_{catalyst}/(g_{EtOH}/h)$

Coke is mainly formed from ethylene decomposition reaction at the beginning of the reaction, which is more favoured at low temperatures, before it deactivates and slows down producing coke. The quantity of coke produced at 650°C is low and it followed a different formation route.

3.2.2 S/E molar ratio

For what it concerns the S/E molar ratio, catalyst stability depends on whether the process is at kinetic or thermodynamic regime.

For thermodynamic regime the catalyst does not deactivate in the 4 h run and for this reason the S/E molar ratio only affects the yield of the products but ethanol conversion and products yield remain constant with time on stream for all the S/E molar ratio studied range. This can be seen in Figs 26 and 27 for a temperature of 600°C, 0.1 $g_{catalyst}/(g_{EtOH}/h)$ and a S/E of 3 and 9, respectively.

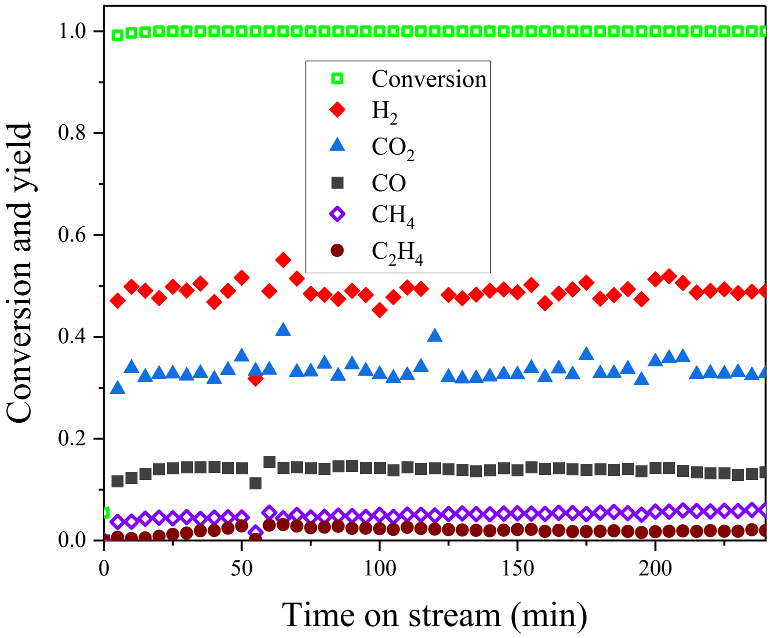

Figure 26: Time on stream with a S/E=3, T=600°C and 0.1 $g_{catalyst}/(g_{EtOH}/h)$

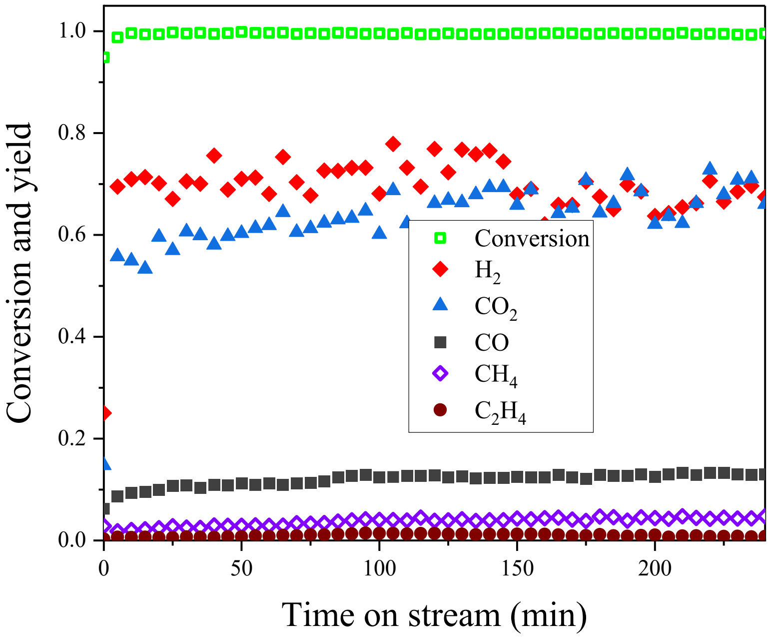

Figure 27: Time on stream with a S/E=9, T=600°C and 0.1 $g_{catalyst}/(g_{EtOH}/h)$

However, when in kinetic regime the S/E molar ratio affects catalyst stability. For higher value of S/E molar ratio yields of products and ethanol conversion remain stable while with less quantity of water the deactivation of ethylene decomposition reaction occurs, leading to a lower hydrogen yield compared to the one at the beginning of the reaction. This behaviour is showed when comparing prior Fig. 23 for a space time of 0.025 $g_{catalyst}/(g_{EtOH}/h)$ at 600°C and a S/E of 3 and in Fig. 28 for a S/E of 9.

The quantity of deposited coke is higher at higher space time and coke formation decreases with the increase of water in the feed, for both kinetic and thermodynamic regime, as it can be seen in Fig.29.

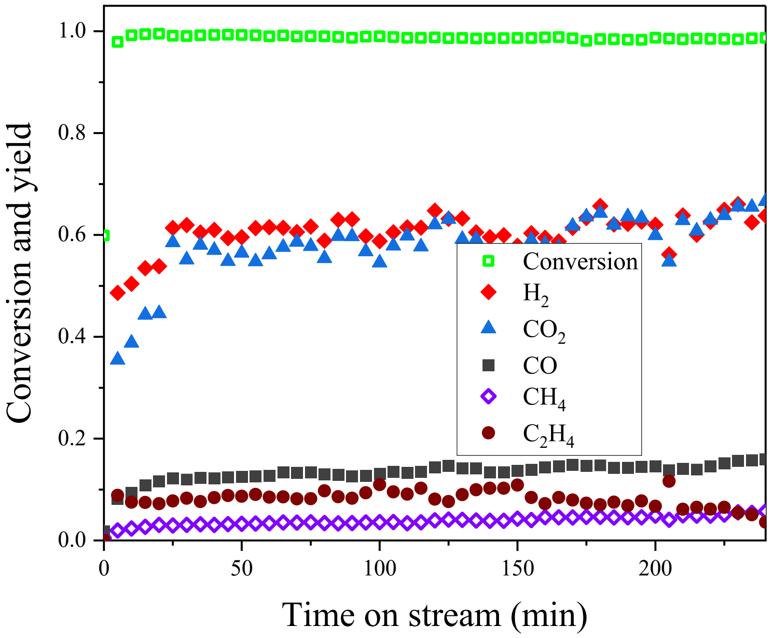

Figure 28: Time on stream with a S/E=9, T=600°C and 0.025 $g_{catalyst}/(g_{EtOH}/h)$

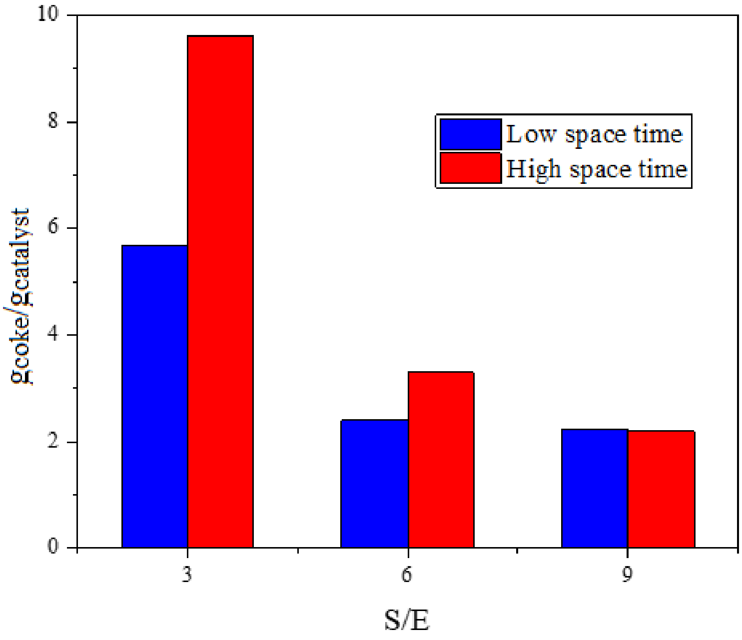

Figure 29: Quantity of coke per gram of catalyst after 4h reaction with different S/E molar ratio, T=600°C for low space time (0.01 $g_{catalyst}/(g_{EtOH}/h)$) and high space time (0.1 $g_{catalyst}/(g_{EtOH}/h)$)

3.2.3 Space time

The value of space time has showed to affect catalyst stability and the trends in products yields with time on stream, as showed in Figs. 30 and 31 for a S/E of 3, 500°C and 0.01 $g_{catalyst}/(g_{EtOH}/h)$ and 0.2 $g_{catalyst}/(g_{EtOH}/h)$ respectively. At the beginning, for low value of space time, the quantity of ethylene is low but after some time its yield increases and at the same time the one of hydrogen decreases. This is because at lower space time the deactivation of ethylene decomposition occurs faster and ethylene is then a major product in the reaction medium because its disappearance by decomposition is stopped. On the other hand, for space time higher than 0.1 $g_{catalyst}/(g_{EtOH}/h)$ the trend of ethylene is not present because with higher value of space time deactivation has not taken place in the first 4 h of reaction.

The quantity of deposited coke, as it can be seen in Fig. 32, doesn't have a monotone behaviour. At low space time, the reaction of ethylene decomposition produces carbon that quickly deactivates the reaction. As ethylene decomposition is one of the main causes of coke deposition as soon as it stops occurring the coke is not produced anymore. For this reason, in kinetic regime, lower is the value of space time, quicker is ethylene decomposition deactivated, lower is the quantity of coke produced per gram of catalyst. In thermodynamic regime, on the contrary, higher value of space time showed lower quantity of coke deposited, that is consisted with literature (Vicente et al. 2014a).

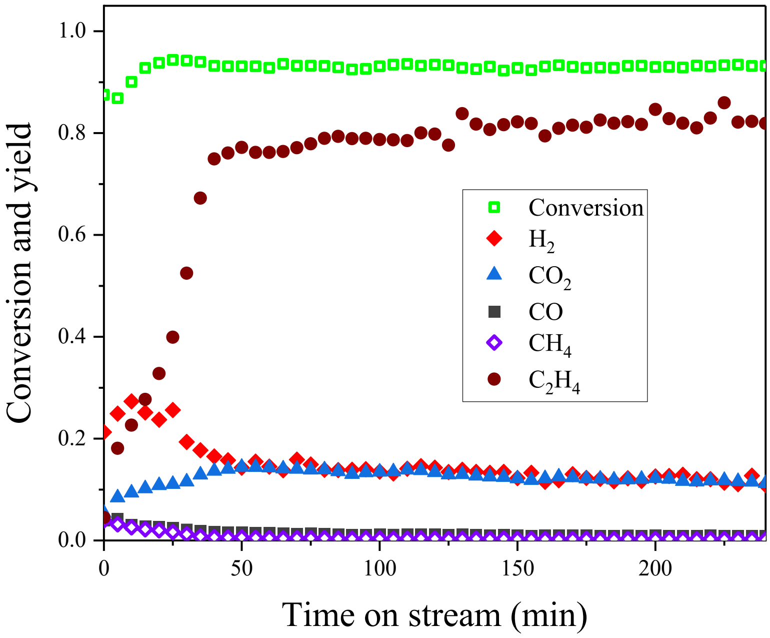

Figure 30: Time on stream with a S/E=3, T=500°C and 0.01 $g_{catalyst}/(g_{EtOH}/h)$

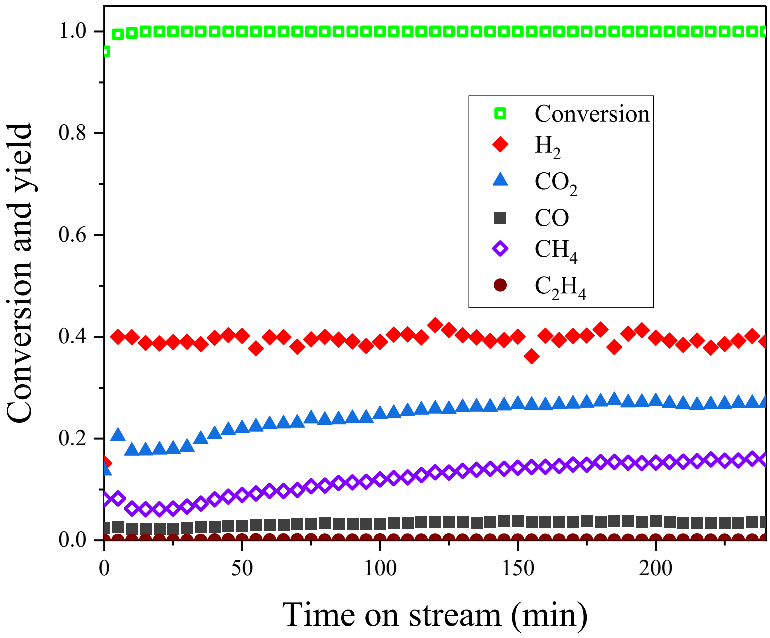

Figure 31: Time on stream with a S/E=3, T=500°C and 0.2 $g_{catalyst}/(g_{EtOH}/h)$

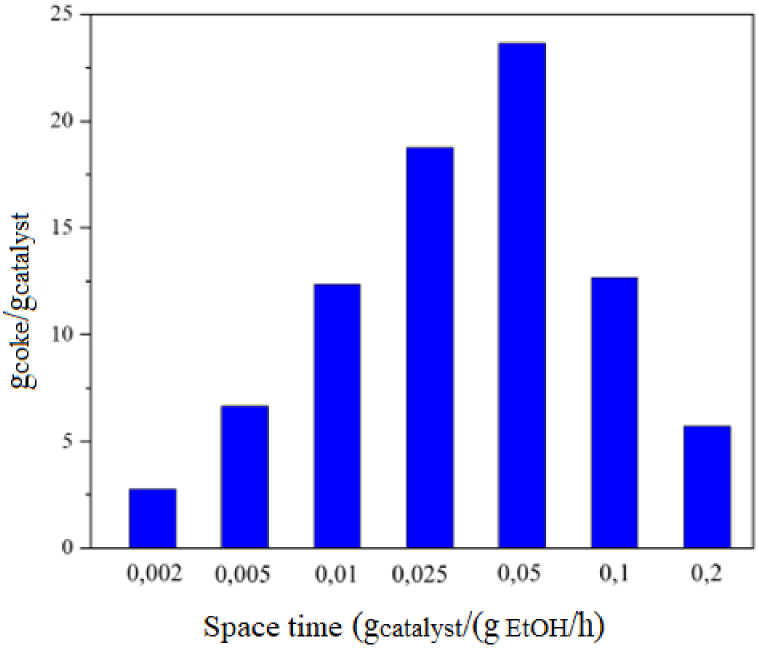

Figure 32: Quantity of deposited coke per gram of catalyst after 4 hours reaction for a S/E =3, 500°C and different space time.

3.2.4 Long duration runs

To better understand the effects of catalyst deactivation, longer runs were performed, showing the evolution of products yields and ethanol conversion during 48 h, at two different temperatures (T=500 °C and T=600°C), a S/E=3 and a space time of 0.1 $g_{catalyst}/(g_{EtOH}/h)$.

In Fig. 33 the evolution with time at 500 °C is represented. Two steps can be noted in the yield of C_2H_4. The increase in the yield of ethylene coincides with a decrease in methane and hydrogen yield. In Fig. 34 instead the evolution with time on stream at a higher temperature (T=600°C) is represented. In this case there is only one step in the increase in the yield of ethylene.

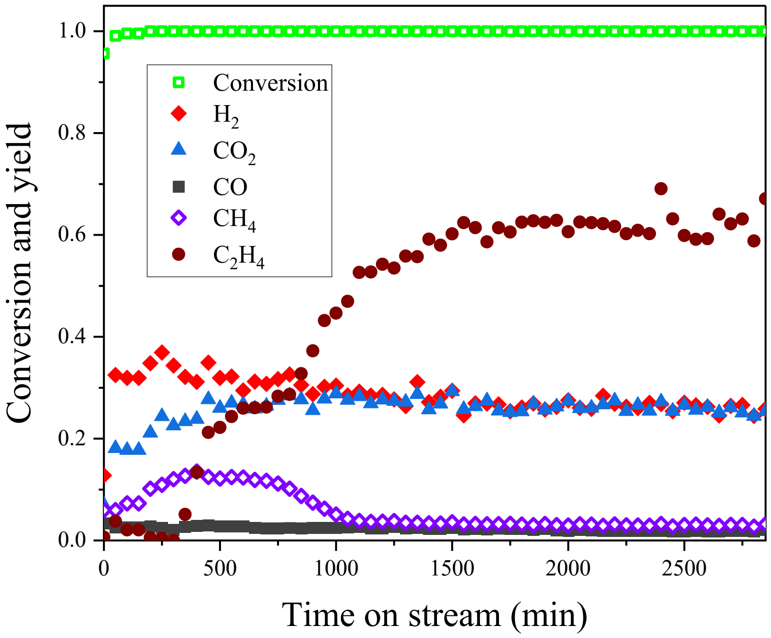

Figure 33: Conversion and yield of products for T=500°C, S/E=3 and space time of 0.1 $g_{catalyst}/(g_{EtOH}/h)$

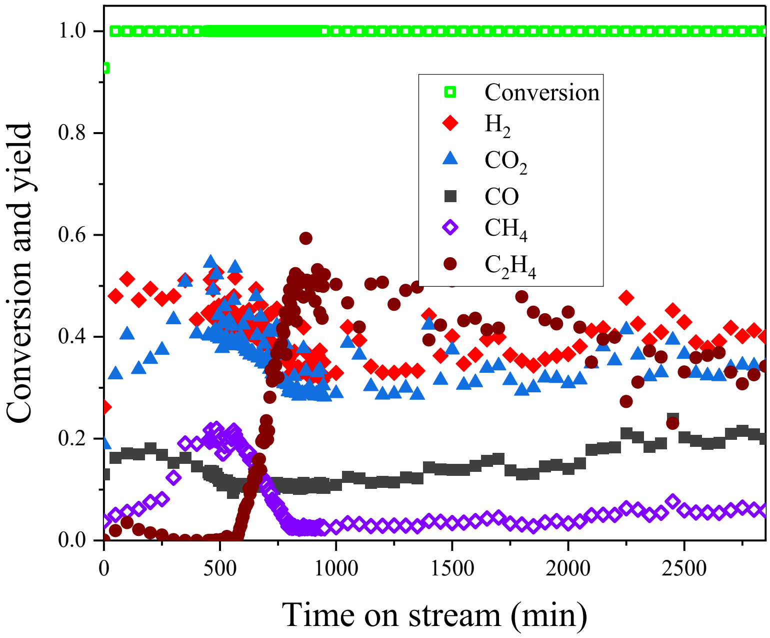

Figure 34: Conversion and yield of products for T=600°C, S/E=3 and space time of 0.1 $g_{catalyst}/(g_{EtOH}/h)$

In both cases, a complete ethanol conversion is reached and does not diminish along the process. This is because at these values of temperatures and space time, the reaction, due to thermodynamically favorable conditions, completes ethanol conversion, by ethanol dehydration, decomposition or steam reforming reactions that continue to be present. On the other hand, the yields of the products are affected by ethylene decomposition reaction deactivation that leads to an increase in ethylene yield and a decrease in hydrogen yield. It shows that metal remains active during the reaction, despite the carbon deposited on the particles: at both temperatures the catalyst is not fully deactivated because the steam reforming reaction still takes place, producing significant yields of H_2 and CO_2, but the quantity of by-products as C_2H_4 increases.

3.3. Effect of coke deposition

One of the main issues with Ni based catalyst for ethanol steam reforming reaction is the deactivation due to coke deposition (Wang, 2009). Moreover, acid support is highly active for ethanol dehydration reaction and for this reason the quantity of ethylene produced with ethanol dehydration (Eq 3) is high and ethylene is one of the main causes of coke deposition with this catalyst. At the beginning, when the catalyst is fresh, ethylene formation is followed by ethylene decomposition (Eq 18) with the formation of hydrogen and coke. This coke causes catalyst deactivation that does not favor further ethylene decomposition, and for this reason the yield in hydrogen becomes lower and the one of ethylene higher with time on stream.

To better understand the route of ethylene formation and polymerization and the decrease in the extent of the second reaction due to catalyst deactivation, only ethylene was fed in the reactor to see if the behavior was the same of the previous SRE reactions. As showed in Fig. 35, ethylene yield follows the same trend that was showed in the previous test with ethanol: at the beginning ethylene decomposes to C and hydrogen and the conversion of ethylene is high. After some time coke formation causes catalyst deactivation, ethylene is no more converted and its yield increases consistently. The hydrogen is no more produced by ethylene decomposition and so its yield decreases as soon as the one of ethylene increases.

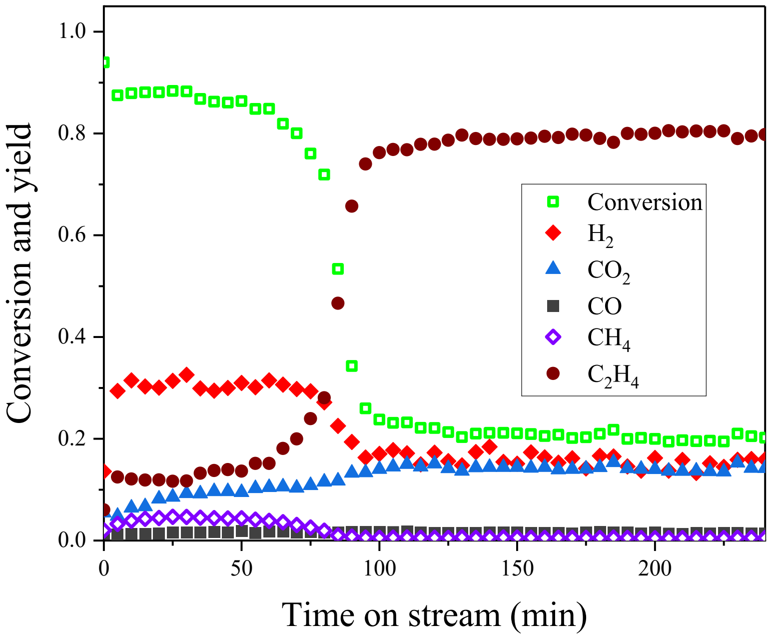

Figure 35: Conversion and yield of products in the steam reforming of ethylene for T=500°C, S/ethylene=3 and space time of 0.0411 $g_{catalyst}/(g_{EtOH}/h)$

To assure that ethylene is the main cause of coke formation we can compare the trend of the yield of ethylene with the mol of the C of the carbon species present in the stream at the reactor outlet and that are not remaining in the reactor, deposited as carbonaceous solid. Fig. 36 shows these trends for a temperature of 500 °C, with S/E=3 and a space time of 0.1 $g_{catalyst}/(g_{EtOH}/h)$. It is evident that coke formation is related to ethylene decomposition: when the yield in ethylene increases, the quantity of carbon molecules that deposited on the catalyst decreases.

The fact that coke deposition does not lead to complete deactivation of the catalyst is linked to the morphology of carbon deposited. In fact, the coke produced from ethylene decomposition is a filamentous carbon that primarily consisted of multiwalled CNTs. CNTs not only have a lower effect on catalyst deactivation but they have their own market that can increase the profitability of the process.

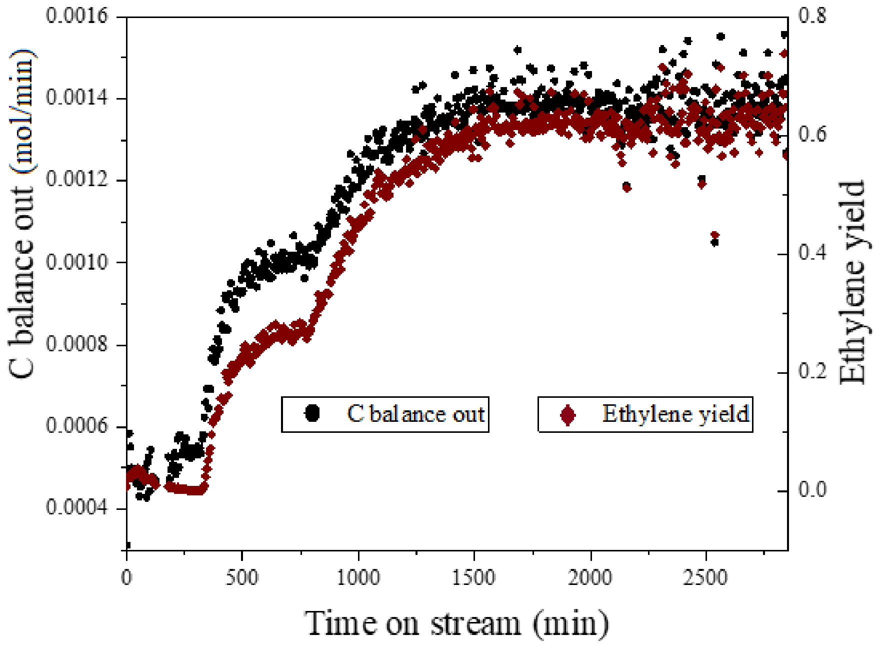

Figure 36: Ethylene yield and quantity of C in mol/min with time on stream at 500°C, S/E=3 and 0.1 $g_{catalyst}/(g_{EtOH}/h)$.

3.4. Reaction pathway proposed

Operating conditions have a complex effect on the reaction, due to the numerous parallel reactions that occur. The kinetic scheme proposed in Fig. 37 shows the main reactions that take place with the use of $NiAl_2O_4$ spinel derived catalyst. The main reaction steps include: ethanol dehydration (Eq. 3) to ethylene followed by ethylene decomposition to coke or ethylene steam reforming to CO, ethanol steam reforming (Eq. 5), WGS reaction and methane steam reforming. Coke formation is mainly caused by ethylene decomposition and Boudouard reaction (Eq. 19). Acetaldehyde formation through ethanol dehydrogenation (Eq. 2) is very slow for all temperature range studied except for the higher temperature studied (650 °C). If it is formed, it exists only as an intermediate and quickly reacts to produce methane or carbon dioxide. Ethanol dehydration has an important role in the reaction pathways, while ethylene decomposition is affected by catalyst deactivation. The reaction pathway mostly depends on temperature, that favours different route based on thermodynamic equilibrium.

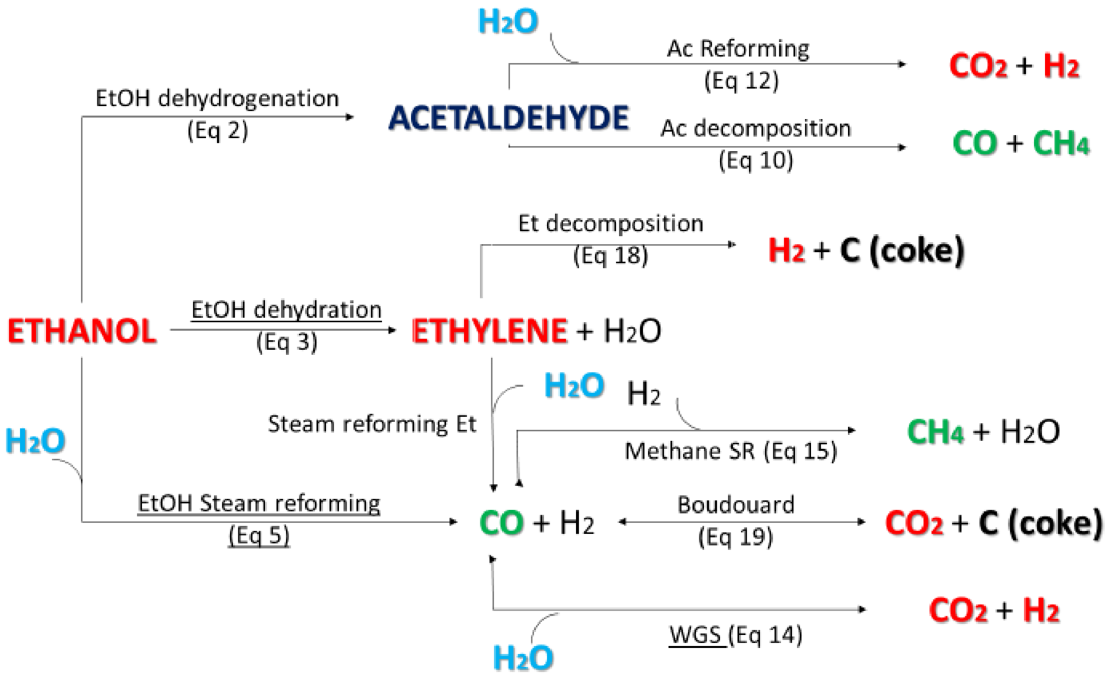

Figure 37: Kinetic scheme proposed for the SRE process over a $NiAl_2O_4$ spinel derived catalyst

4. CONCLUSIONS

The $NiAl_2O_4$ spinel derived catalyst reduced at 850 °C has proved to be very active for the SRE reaction, with ethanol conversion almost complete for temperature above 500 °C and space time above 0.025 $g_{catalyst}/(g_{EtOH}/h)$ and a good hydrogen yield when working in optimum conditions.

Temperature is the condition that most affects the selectivity of the reaction. From this experimental study we can conclude that the range of temperature with the best performance for this catalyst is 500° - 600°. This is because an increase in temperature favors ethanol dehydration, WGS reaction and methane steam reforming, leading to higher conversion of ethanol and hydrogen production. At higher temperature, however the WGS reaction equilibrium shifts towards the left, leading to poor performance.

Increasing the S/E molar ratio has a beneficial effect on the conversion and hydrogen production, and its effect is higher at low value of S/E molar ratio, while from 6 to 9 does not affect a lot. Increasing the quantity of water also increases the operation cost, so an economical study for this reaction must be done to choose the optimum value.

A space time above 0.1 $g_{catalyst}/(g_{EtOH}/h)$ is needed not only to have good conversion but also due to catalyst stability. In fact, with low value of space time the catalyst quickly deactivates and ethylene does not react to form hydrogen.

To have better performance (higher H_2 yield, complete ethanol conversion, good catalyst stability), the following operating conditions are recommended: 600 °C, space time above 0.1 $g_{catalyst}/(g_{EtOH}/h)$ and S/E molar ratio = 9. Under these conditions, a H_2 yield of 74% is achieved, which remains high on time on stream.

Moreover, the coke deposition does not affect a lot the catalyst that does not deactivate completely and it is in the form of CNTs that can have a commercial interest.

The $NiAl_2O_4$ spinel derived catalyst reduced at 850°C in general has good performance for SRE. However, after it has been used it is not possible to regenerate it. For this reason, more studies on how to avoid this phenomenon are needed.

5. NOMENCLATURE

F_E = ethanol molar floe at reactor outlet

F_{EO} = ethanol molar floe at reactor inlet

Fi= molar flow rate of product i

X_{Eth} = Ethanol conversion

Y_i = Product yield

Acronymous

CNTs = Carbon Nanotubes

S/E = steam to ethanol molar ratio

SRE = ethanol steam reforming

WGS = Water Gas Shift

Greek letter

ν = stoichiometric coefficient between product i and ethanol

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