In Situ Capture Of CO_2 In The Steam Reforming Of Ethanol Over Ni/SiO_2 Catalyst For Hydrogen Production

Jorge Vicente*, Aingeru Remiro, Alaitz Atutxa, Javier Ereña, Ana G. Gayubo,
Javier. Bilbao
Dpto. Ingeniería Química, Universidad del País Vasco, Apdo 644, 48080 Bilbao, Spain
Corresponding author e-mail: jvicente003@ikasle.ehu.es

The improvement in ethanol steam reforming to produce H_2 by in situ CO_2 capture has been studied in a fluidized bed using a Ni/SiO_2 catalyst and calcite and dolomite as sorbents. Both sorbents have been agglomerated with laponite in order to improve their fluidodynamic behavior and resistance to attrition. The CO_2 sorption capacity of calcite (analyzed by thermogravimetry) is higher than that of dolomite, but dolomite shows higher fractional conversion of CaO to $CaCO_3$ than calcite due to the larger pore volume produced during the calcination of $MgCO_3$. The kinetic runs carried out at 500 °C with both sorbents show that in situ CO_2 capture displaces the steam reforming reaction, but other parallel reactions such as ethanol decomposition, WGS and CH_4 steam reforming are not affected by CO_2 removal. Consequently, hydrogen yield increases whereas CH_4 and CO yields remain almost constant. For both sorbents, saturation with CO_2 is achieved after 20 min time-on-stream, which indicates that sorption-enhenced steam reforming must be carried out under successive carbonatation-decarbonatation steps, in order to recover CO_2 sorption capacity of the sorbent.

1. Introduction

The production of hydrogen from steam reforming of alcohols promotes the use of hydrogen as an alternative fuel, because it does not require hydrogen storage and distribution (Batista et al., 2003), which are the most important drawbacks to the use of hydrogen as an alternative source of energy. Moreover, alcohols are easily decomposed in the presence of water and generate a H_2-rich mixture free from sulphur, suitable for feeding fuel cells (Fierro et al., 2002).

In comparison with other fuels, ethanol presents a series of advantages for eteam reforming (Liberatori et al., 2007): i) the thermodynamic properties allow high ethanol conversion at low temperature ii) it represents a renewable and CO_2-neutral fuel that can readily be obtained from biomass fermentation; iii) it is easy to store, handle and transport in a safe way due to its low toxicity and volatility and iv) the infrastructure required for its distribution is similar to the conventional gas stations.

Ethanol can be efficiently converted into H_2 by catalytic steam reforming (1):

$$C_2H_5OH + 3\ H_2O \Leftrightarrow 6\ H_2 + 3CO_2 \tag{1}$$

However, many possible reaction pathways take place during ethanol steam reforming, such as ethanol decomposition (2), CH_4 steam reforming (3), WGS reaction (4):

$$C_2H_5OH \Leftrightarrow CH_4 + CO + H_2 \tag{2}$$

$$CH_4 + 2 H_2O \Leftrightarrow 4 H_2 + CO_2 \tag{3}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{4}$$

Ethanol dehydration to ethylene and ethanol dehydrogenation to acetaldehyde are also important reaction pathways at low temperature. Consequently, other undesirable products (mainly CH_4 and CO) may be formed together with H_2 and CO_2 in the reaction, so several processes are used to increase the hydrogen yield and selectivity. Sorption-enhanced hydrogen production may accomplish reforming, WGS and purification in a single processing step (Yi and Harrison, 2005). The use of a sorbent for CO_2 removal mixed with the catalyst leads to i) an increase in the conversion of ethanol and hydrogen purity by eliminating the thermodynamic limitations at a given operating condition (Mondal et al., 2005), ii) provide a chance to sequestrate the greenhouse gas and release it almost pure when the sorbent is regenerated and iii) a partial compensation of energy requirements of the endothermal reforming reactions due to the exothermal nature of the carbonatation (Satrio et al., 2007).

The advantages of in situ CO_2 collection have been experimentally verified in the steam reforming of methane (in fixed and fluidized bed) (Balasubramanian et al., 1999; Johnsen et al., 2006), but there are no experimental evidences of the use of an adsorbent for steam reforming of other feeds. Therefore, the aim of this paper has been to improve the selectivity and yield of hydrogen by means of in situ CO_2 capture in ethanol steam reforming over a Ni/SiO_2 catalyst, whose performance for ethanol steam reforming has been proven to be successful.

2. Experimental

2.1 Catalyst preparation and characterization

The Ni/SiO_2 catalyst has been prepared by impregnating the support with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (CARLO ERBA Reagents, 99% purity), followed of drying at 110 ºC overnight and calcination at 550 ºC for 4 h in air. The catalyst has a specific surface area of 285 m^2/g and a nickel content of 10 wt%. TPR profiles showed 500 ºC is enough to carry out the reduction of the catalyst before the kinetic experiments. The dispersion degree of nickel on the catalyst, determined by H_2 chemisorption, is relatively low (2.3 %), as typically observed for high Ni content catalysts.

2.2 Sorbent preparation

Calcite and dolomite (Calcinor) have been used as sorbents for CO_2 capture. Since both materials are structurally weak and not easily handled without serious decrepitation (Satrio et al., 2007), they have been agglomerated with laponite (Rockwood) in order to improve their mechanical resistance and their hydrodynamic properties.

Thus, sorbents with particle size lower than 90 μm were agglomerated with laponite, extruded and dried in air overnight. Finally they were crushed and sieved to a particle size between 90 and 150 μm and then calcined at 800 ºC during 2 h. The final sorbents have been denoted as 10L-C and 20L-D, where the number refers to the laponite content

(wt%). These contents are the optimum in order to attain good hydrodynamic properties and a similar mechanical resistance for both sorbents.

2.3 Sorbent characterization

BET surface area, pore volume and mean pore size of the sorbents have been measured by N_2 adsorption-desorption at 77 K (Micromeritics ASAP 2010). Their CO_2 sorption capacity has been analyzed in a thermobalance (STD 2960 TA Instruments) at different temperatures and atmospheric pressure by the following procedure: the sample (35 mg) is calcined in situ at 800 ºC for 30 min, and subsequently it is saturated at different temperatures with CO_2 by flowing a 40 ml/min of CO_2/He (17 v%) mixture.

The level of carbonatation of the sorbents after the kinetic runs has also been analyzed by calcination in the thermobalance.

2.4 Activity test

Kinetic runs have been carried out in automated reaction equipment provided with an isothermal fluidized-bed reactor with 22 mm of internal diameter connected on-line to a MicroGC Agilent 3000 for product analysis. The hydrodynamic properties of the bed have been improved by mixing the catalyst-sorbent mixture with carborundum (particle size below 60 μm) in a catalyst/sorbent/inert ratio of 1/10/15. The total mass of the bed is 13 g. The operating conditions are: 500 ºC, 1 atm, space time = 8.3 $g_{catalyst}min/g_{EtOH}$ and water/ethanol molar ratio = 6:1. Prior to the runs, the catalyst is reduced at 500 ºC for 2 h with a flow rate of 60 ml min^{-1} of 10% H_2 in He.

3. Results and discussion

3.1 Sorbent characterization

Table 1 shows the BET surface area and pore volume of the samples as-received, calcined and agglomerated and calcined sorbents. Both surface area and pore volume are quite small for as-received samples (nonporous materials) and increase significantly for the calcined samples, due to the porosity created by the release of CO_2 during calcinations. After calcination, dolomite has higher BET surface area and pore volume than calcite. The reduction in BET surface area and pore volume for agglomerated and calcined sorbents is due to the fact that laponite is a nonporous material after calcinations.

It has been proven that laponite does not have any activity for CO_2 capture. Consequently, it behaves as an inert solid in the agglomerated sorbents.

Table 1. BET surface area and pore volume of calcite and dolomite as-received, calcined (at 800 ºC for 2 h) and agglomerated with laponite and calcined.

Sorbent	Composition	S_{BET} (m^2/g)	Pore volume (cm^3/g)
As-received calcite	$CaCO_3$	0.86	0.005
As-received dolomite	$CaCO_3 \cdot MgCO_3$	1.88	0.007
Calcined calcite	CaO	20.46	0.175
Calcined dolomite	CaO (63 wt%)·MgO	25.64	0.263
Calcined 10L-C	CaO+Laponite	17.94	0.147
Calcined 20L-D	CaO·MgO+Laponite	19.36	0.196

Table 2. CO₂ sorption capacity (C, $g_{CO2}/g_{sorbent}$) and fractional conversion of CaO (X) at different temperatures for calcined calcite and dolomite.

	300 ºC		400 ºC		500 ºC		600 ºC		700 ºC	
	C	X	C	X	C	X	C	X	C	X
Calcite	0.098	0.125	0.199	0.253	0.430	0.547	0.507	0.645	0.522	0.664
Dolomite	0.063	0.129	0.173	0.352	0.412	0.840	0.428	0.871	calcination	

The CO₂ sorption capacity at different temperatures, (C), and the corresponding fractional conversion of CaO (X, defined as mol of CaCO₃ formed by carbonatation per mol of the nominal CaO content in the sorbent) are set out in Table 2 for both calcined sorbents. It is observed that CO₂ capture for calcined calcite is enhanced by the increase in temperature up to 700 ºC. Nevertheless, the highest sorption capacity for dolomite is obtained at 600 ºC and calcination takes place at higher temperatures. Moreover, at 500 ºC the sorption capacity of dolomite is close to that of saturation and, consequently, this is the optimum temperature for CO₂ capture for dolomite.

As expected, the CO₂ sorption capacity of calcite is higher than that of dolomite because the thermodynamic equilibrium at these temperatures leads to the decomposition of MgCO₃. However, the fractional conversion of CaO to CaCO₃ for dolomite is higher than that for calcite at any temperature, due to the larger pore volume produced during the calcination of MgCO₃, which provides an improved access of CO₂ to inside of the particle (Silaban et al., 1996).

3.2 Catalytic tests

Figure 1 shows ethanol conversion and products yield obtained in sorption-enhanced ethanol steam reforming at 500 ºC over Ni/SiO₂ catalyst using 10L-C (left) and 20L-D (right) as sorbents. For these operating conditions ethanol conversion is complete even after saturation of the sorbents (often referred as the post-breackthough period). Apart from H₂ and CO₂, significant amounts of CH₄ and CO are obtained, but only traces of other by-products (such as acetaldehyde or acetone) have been observed. These results prove that the decomposition of ethanol to CH₄ and CO, eq.(2), is an important secondary reaction in ethanol steam reforming. Moreover, the lower yield of CO compared to that of CH₄ indicates that WGS reaction also occurs in parallel to steam reforming, whereas CH₄ steam reforming is not enhanced at this temperature.

The benefit of in situ CO₂ capture during ethanol steam reforming is clearly observed in both graphs in Figure 1. The CO₂ removal shifts the equilibrium of ethanol steam reforming and, consequently, hydrogen yield increases from 3.2 mol_{H2}/mol_{EtOH} (value corresponding to the sorbent saturation with CO₂) up to 3.6 mol H_2/mol_{EtOH} during the pre-breackthough period, independiently of the sorbent used. However, CO and CH₄ yields remains almost constant, which indicates that CO₂ capture does not shift WGS reaction nor methane reforming, as the Ni/SiO₂ catalyst used is not very active for these reactions compared to its activity for ethanol steam reforming. The breakthrough time for both sorbents is about 21 min under these operating conditions. After this period, the reaction enhancement is lost because no CaO is available to react with CO₂ and, consequently, decarbonatation has to be performed to reactivate the sorbent. Thus, the sorption-enhenced ethanol steam reforming requires cyclic operation under successive carbonatation-decarbonatation steps for the sorbent.
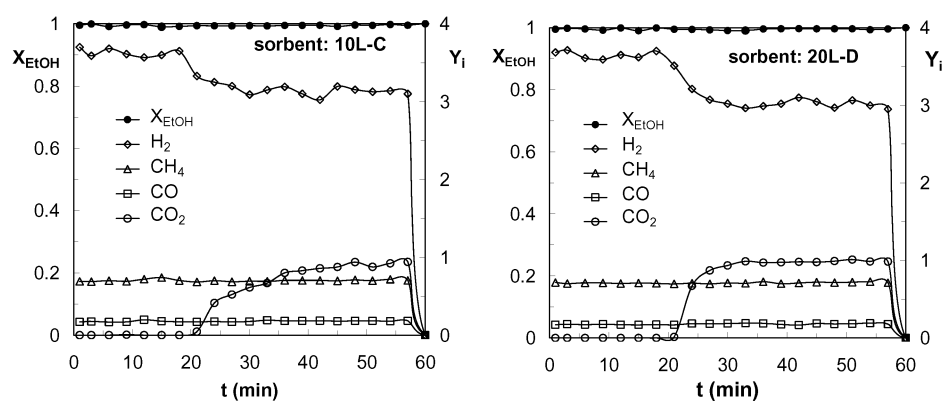
Figure 1. Ethanol conversion and products yield in sorption-enhanced ethanol steam reforming over Ni/SiO$_2$ catalyst using 10L-C (left) and 20L-D (right) as sorbents. Operating conditions: 500 °C; 1 atm; 8.3 g$_{cat}$min/g$_{EtOH}$; water/ethanol molar ratio= 6/1.

The rate of carbonatation observed in Figure 1 is slightly different for both sorbents. Dolomite based sorbent (right graph) achieves the saturation equilibrium shortly before calcite based sorbent (left graph), probably due to a better accessibility of CO$_2$ towards CaO, thanks to the higher pore volume created by MgCO$_3$ decomposition. Subsequent to the kinetic runs, the level of carbonatation achieved by both sorbents has been measured by thermogravimetry. The fractional conversion of CaO was 0.545 for 10L-C and 0.789 for 20L-D, which are quite close to those shown in Table 2 for 500 °C.

4. Conclusions

Hydrogen yield in the ethanol steam reforming is enhanced by in situ CO$_2$ capture with calcite or dolomite as sorbents. Both solids need to be agglomerated with a binder, such as laponite, in order to improve their fluidodynamic behavior and mechanical resistance in a fluidized bed. 500 °C is a suitable temperature for CO$_2$ capture with dolomite, while calcite is efficient for CO$_2$ capture up to 700 °C. The CO$_2$ sorption capacity of dolomite is lower than that of calcite, but dolomite shows higher fractional conversion of CaO to CaCO$_3$ due to the larger pore volume produced during the calcination of MgCO$_3$.

The CO$_2$ capture with both calcite and dolomite sorbents in the ethanol steam reforming shifts the equilibrium and increases hydrogen yield, whereas CO and CH$_4$ yields remain almost constant. Dolomite based sorbent saturates with CO$_2$ slightly more rapid than the calcite based sorbent. Nevertheless, taking into account the need for performing carbonatation-decarbonatation cycles, 20L-D sorbent is more suitable than 10L-C sorbent due to the reported better performance of dolimite compared to that of calcite in the cyclic operation (Silaban et al., 1996).

References

Balasubramanian B., Lopez A., Kaytakoglu S. and Harrison D.P., 1999, Hydrogen from methane in a single-step process, Chemical Engineering Science 54, 3543-3552.

Batista M.S., Santos R.K.S., Assaf E.M., Assaf J.M. and Ticianelli E.A., 2003, Characterization of the activity and stability of supported cobalt catalysts for the steam reforming of ethanol, Journal Power of Sources 124, 99-103.

Carreño N.L.V., Garcia I.T.S., Raubach C.W., Krolows M., Santos C.C.G., Probst L.F.D. and Fajardo H.V., 2008, Nickel-carbon nanocomposites prepared using castor oil as precursor: A novel catalyst for ethanol steam reforming, Journal of Power Sources, doi: 10.1016/j.jpowsour.2008..12.004

Fierro V., Klouz V., Akdim O. and Mirodatos C., 2002, Oxidative reforming of biomass derived ethanol for hydrogen production in fuel cell applications, Catalysis Today 75, 141-144.

Liberatori J.W.C., Ribeiro R.U., Zanchet D., Noronha F.B. and Bueno J.M.C., 2007, Steam reforming of ethanol on supported nickel catalysts, Applied Catalysis A: General 327, 197-204.

Mondal K., Piotrowski K., Dasgupta D., Hippo E. and Wiltowski T., Hydrogen from coal in a single step, Ind. Eng. Chem. Res. 44, 5508.

Satrio J.A., Shanks B.H. and Wheelock T.D., 2007, A combined catalyst and sorbent for enhancing hydrogen production from coal or biomass, Energy & Fuels 21, 322-326.

Silaban A., Narcida M. and Harrison D.P., 1996, Characteristics of the reversible reaction between CO_2 (g) and calcined dolomite, Chem. Eng. Comm. 146, 149-162.

Jhonsen, K., Ryu, H.J., Grace, J.R. and Lim, C.J., 2006, Sorption-enhanced steam reforming of methane in a fluidized bed reactor with dolomite as CO_2-acceptor, Chemical Engineering Science 61, 1191-1198.

Yi K. and Harrison D.P., 2005, Low-pressure sorption-enhanced hydrogen production, Ind. Eng. Chem. Res. 44, 1665-1669.