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# Toluene steam reforming using coprecipitated Ni/Al catalysts modified with lanthanum or cobalt

Sergio Bona, Patricia Guillén, J. Germán Alcalde, Lucía García*, Rafael Bilbao

*Aragon Institute of Engineering Research, Department of Chemical and Environmental Engineering,*
*University of Zaragoza, María de Luna 3, 50018 Zaragoza, Spain*

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## Abstract

Toluene has been chosen as a model compound of biomass gasification tar and its destruction has been studied by steam reforming. The experiments have been performed in a bench scale installation that uses a fluidized bed reactor with a technology very similar to the Waterloo Fast Pyrolysis Process (WFPP). All the experiments have been carried out at 650 °C and atmospheric pressure. Ni/Al/La catalysts with La/Ni ratios of 0, 0.044, 0.088 and 0.13 have been tested, the middle two showing the best performance. Ni/Co/Al catalysts with Co/Ni ratios of 0, 0.025, 0.10 and 0.25 have also been tested. The Ni/Co/Al catalyst with the best results is that with a Co/Ni ratio of 0.10. For the Ni/Co/Al catalyst with Co/Ni = 0.10, the influence of the steam/carbon molar (S/C) ratio on gas yields has been studied for values from 5.5 to 1.5. Yields of $H_2$ and $CO_2$ decrease, while $CH_4$ and CO yields increase when the S/C ratio diminishes. The influence of the catalyst weight/toluene flow rate ($W/m_t$) ratio has been analyzed for Ni/Al/La catalyst with a La/Ni ratio of 0.088 and Ni/Co/Al catalyst with Co/Ni = 0.10. For both catalysts, carbon conversion to gas, total gas, $H_2$ and $CO_2$ yields increase when the $W/m_t$ ratio increases.

*Keywords:* Toluene; Biomass tar; Steam reforming; Ni/Al catalysts; Lanthanum; Cobalt

## 1. Introduction

Gasification of biomass is a promising technology for power generation or chemical production. One of the main inconveniences for commercialising biomass gasification is the product gas quality. Among the impurities present in product gas, tar represents a serious impediment that has received significant attention in literature [1–4].

Tar can be deposited on surfaces in filters, heat exchangers and engines, reducing component performance and increasing maintenance requirements. It must also be remembered that tar can polymerize to form more complex structures and aerosols.

Tar removal methods can be classified as primary or secondary [2]. Primary methods include all the measures taken in the gasification step itself to prevent tar from being formed in the gasifier or to convert it. Secondary methods can be chemical or physical treatments downstream the gasifier. Both primary and secondary methods include the use of bed additives. These can be metallic catalysts, mainly Ni-based catalysts [5–10], dolomites [11–14], olivines [13,15] or a combination of metals on dolomite or olivine [16–19]. Metallic catalysts have the advantage of being more active at low temperatures but they can suffer the inconvenience of deactivation caused mainly by carbon deposits. Some reviews in the literature have presented catalysts for biomass tar destruction and a more detailed description of these catalysts can be found elsewhere [20–22].

Tar formed in the thermochemical processing of biomass is a complex mixture of organic compounds. Therefore, tar removal studies usually consider the use of model compounds, examples of which include phenol [23,24], naphthalene [25–27] and toluene [19,26,28–30]. In the present work, toluene has been chosen as a model compound of biomass gasification tar because it is found in significant quantities, especially at relatively low temperatures (700 °C), being surpassed only by benzene [31]. Toluene has been chosen rather than benzene due to the higher reactivity of the latter [26]. Simell et al. [28] concluded that a realistic picture of the tar-decomposition activity of catalysts could be achieved with toluene.

A variety of catalysts and operating conditions have been described in works about toluene decomposition. Simell et

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* Corresponding author. Tel.: +34 976 762194; fax: +34 976 761879.
*E-mail address:* luciag@unizar.es (L. García).

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al. [28] studied toluene decomposition using limestones and dolomites in a fixed bed reactor at 900 °C and 2 MPa. In 1997, Simell et al. [29] studied toluene and ammonia decomposition in a fixed bed reactor at 900 °C and pressures of 2 and 5 MPa, using several materials: $Al_2O_3$, dolomite and a nickel catalyst. Coll et al. [26], in a fixed bed reactor and at temperatures of 700 °C and higher, studied toluene conversion using two commercial catalysts (ICI 46-1 and UCI G90-C). They also analyzed the influence of steam/carbon (S/C) molar ratios from 2.5 to 6.5. Wang and Gorte [32], also in a fixed bed reactor using a S/C ratio of 2 and temperatures from 350 to 500 °C, analyzed Pd/ceria, Pt/ceria and Pd/alumina catalysts. Srinakruang et al. [17] employed a Ni/dolomite catalyst at temperatures from 675 to 775 °C in a fixed bed reactor. Juutilainen et al. [30] tested several catalysts (dolomite, zirconia materials, $Al_2O_3$, $ZrO_2/Al_2O_3$ and $NiO/Al_2O_3$) at temperatures from 550 to 900 °C using a synthetic gasification gas with 3% oxygen. Toluene was steam-reformed using a S/C ratio of 5 at temperatures from 700 to 830 °C and employing Ni/olivine catalysts doped with $CeO_2$ [19].

As mentioned above, nickel catalysts are widely used in biomass gasification and biomass gas cleaning. In order to improve the performance, these catalysts can be appropriated by the incorporation of promoters, such as lanthanum and cobalt.

Lanthanum can be chosen as a promoter because of its beneficial effect for catalytic steam gasification of pine sawdust [33], steam reforming of bio-oil [34] and steam reforming of naphthalene [25]. It is widely known that lanthanum improves the stability of the catalyst and decreases carbon formation [35,36].

The presence of cobalt in the catalyst has shown good results in steam reforming of bio-oil [34]. Titania-supported cobalt and nickel bimetallic catalysts have been studied in carbon dioxide reforming of methane [37], and cobalt catalysts have also been employed in steam reforming of naphthalene [27]. The use of cobalt as a promoter has been demonstrated to cause a decrease of carbon deposits on catalysts [38,39].

In this context, it has been considered of interest to study the performance of coprecipitated nickel-alumina catalysts promoted with lanthanum or cobalt in a fluidized bed reactor at a relatively low temperature: 650 °C. In the present work, we analyze the influence of the promoter content in the catalyst in order to select the appropriate amount. The influence of the steam/carbon (S/C) molar ratio is analyzed for the Ni/Co/Al catalyst with a Co/Ni ratio of 0.10. The S/C ratio has been varied from 5.5 to 1.5.

The influence of the catalyst weight/toluene flow rate ratio has been studied for the catalysts with the better performance: Ni/Al/La catalyst with a La/Ni ratio of 0.088 and Ni/Co/Al catalyst with a Co/Ni ratio of 0.10.

## 2. Experimental

### 2.1. Experimental system

The experimental system is a bench-scale installation using a technology very similar to the Waterloo Fast Pyrolysis Process (WFPP) [40]. A schematic of the installation is shown in Fig. 1.

A fluidized-bed reactor is used. The reactor is made of 316 stainless steel and the distributor plate is made of inconel. The body of the reactor has an inner section of 13.14 cm$^2$. The reactor has a lateral arm containing an adjustable feeding injection system. This feeding system is composed of four concentric tubes. Toluene is introduced by the inner tube, while the second tube delivers nitrogen and water. The outer tubes are used as a cooling jacket. The feeding system is designed to produce an appropriate dispersion at the feeding point and prevents thermal decomposition of the toluene before it reaches the reaction bed.

Toluene is delivered by a HPLC metering pump, P01, AGILENT series 1100, with flow rates up to 5 ml/min. The water needed for reaction is distilled water that enters the reactor via a peristaltic pump PERICOR CR240, P02. The gases needed in this installation (air for cleaning the reactor, hydrogen for reducing the catalyst, and nitrogen) are metered by mass flow controllers.

A cyclone is used to clean the product gas of solid particles that may be elutriated from the bed. The water and toluene that have not reacted together with other possible liquids formed by the reaction are retained in a system of two condensers and a cotton filter. The cotton filter can also retain small solid particles of catalyst or carbonaceous residues.

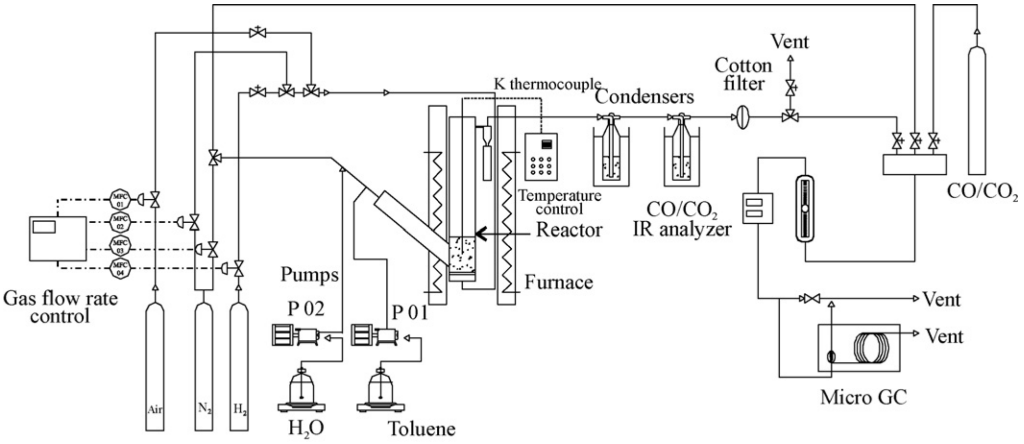

Fig. 1. Schematic of the experimental system.

The CO and $CO_2$ concentrations in the exit gas are continuously determined by an infrared analyzer, ROSEMOUNT BINOS 100. An AGILENT P200 Micro GC is used to measure concentrations of $H_2$, $N_2$, CO, $CO_2$, $CH_4$ and $C_2$ ($C_2H_2$, $C_2H_4$ and $C_2H_6$) in the product gas. Two columns are used with TC detectors, and helium and argon are used as carriers. The time required for the analysis is 3.2 min.

The experimental system worked at atmospheric pressure. All the experiments were carried out at 650 °C and using a nitrogen flow rate of around 2100(STP) $cm^3$/min. For the majority of experiments, performed with a S/C ratio of around 5.7, an inlet toluene-feeding rate, $m_t$, of around 0.17 g/min and a flow rate of water of around 1.3 g/min were used. For lower S/C ratios, the inlet toluene-feeding rate was increased, while the flow rate of water was decreased, maintaining a constant gas flow rate under the reforming conditions. As the inlet toluene-feeding rate was increased, the catalyst weight was also increased in order to obtain a constant catalyst weight/toluene flow rate ($W/m_t$) ratio.

The reaction bed was composed of sand (265 g) and catalyst. The catalyst weight varied from 0 g in the non-catalytic experiment up to 4.32 g in catalytic experiments. This variation was needed for studying the influence of the $W/m_t$ and S/C ratios. The particle sizes of catalyst and sand used were between 160 and 320 μm.

### 2.2. Catalysts

The catalysts were prepared in our laboratory by coprecipitation. The preparation method was similar to that described by Al-Ubaid and Wolf [41]. Seven catalysts were prepared: a Ni/Al catalyst with an atomic Ni:Al ratio of 1:2, three Ni/Al/La catalysts with La/Ni atomic ratios of 0.044, 0.088 and 0.13 corresponding to lanthanum contents of 4, 8 and 12 wt% of $La_2O_3$ (in the calcined catalysts), respectively, and three Ni/Co/Al catalysts with Co/Ni atomic ratios of 0.025, 0.10 and 0.25. Lanthanum was substituted for Al in the Ni/Al/La catalysts because it enhances the properties of the support, while in the Ni/Co/Al catalysts cobalt was substituted for Ni because it is a promoter of the active phase [34]. Ammonium hydroxide was added to a solution of metallic nitrates in distilled water until the final pHs were reached, these being 7.9 for the Ni/Al and Ni/Co/Al catalysts and 8.05 for the Ni/Al/La catalysts. The precipitation medium was maintained at 40 °C and moderately stirred. The precipitate obtained was filtered and washed at 40 °C and dried for about 15 h at 105 °C. Following these steps, the precursor was obtained. All the precursors were calcined in an air atmosphere at 750 °C for 3 h. The calcined catalysts were all reduced in the reactor at a temperature of 650 °C during 1 h using hydrogen diluted in nitrogen ($H_2$:$N_2$ = 1:10). The flow rate of hydrogen was 200 $cm^3$(STP)/min. More details about the catalyst preparation can be found in literature [33,42,43].

The calcined catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption and elemental analysis.

NiO and $NiAl_2O_4$ crystalline phases were identified by XRD in all the catalysts. In the Ni/Al/La catalysts, phases with lanthanum were not detected. In Ni/Co/Al catalysts, $CoAl_2O_4$ may also be present. The two aluminates, $NiAl_2O_4$ and $CoAl_2O_4$, present XRD patterns with the same diffraction angles ($2\theta$) although some intensities are different. XRD patterns of Ni/Al/La catalysts can be found in Ramos et al. [44]. Fig. 2 shows XRD patterns of the Ni/Al and Ni/Co/Al catalysts. When the Co/Ni atomic ratio increases, less signal of NiO at $2\theta = 43.3°$ is observed while the peak can be more clearly appreciated at $2\theta = 31.2°$, corresponding to $CoAl_2O_4$.

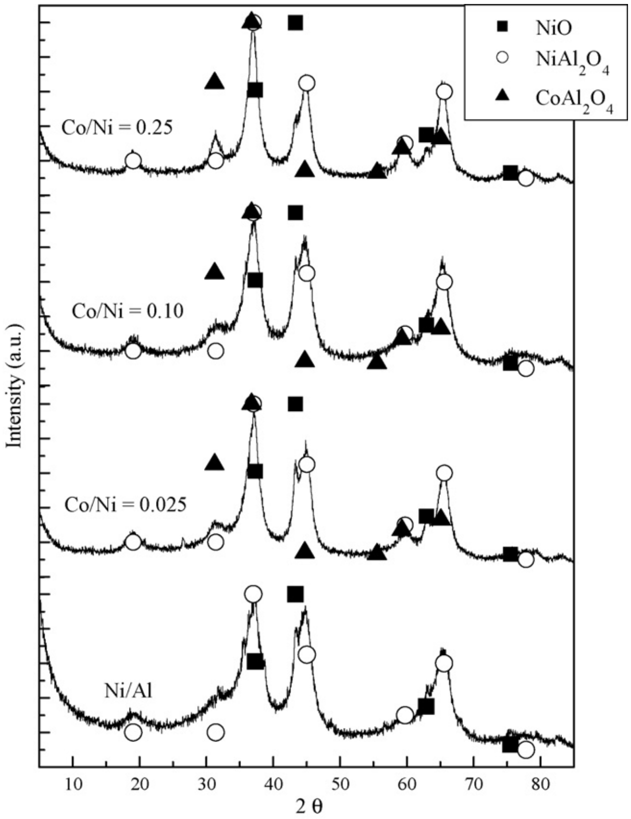

Fig. 2. XRD patterns of Ni/Al and Ni/Co/Al-calcined catalysts.

The surface area of the catalysts, determined by nitrogen adsorption, ranged from 131 to 191 $m^2$/g. It is appreciated that the addition of lanthanum causes a slight decrease in surface area. The maximum surface area was obtained for the Ni/Co/Al catalyst with a Co/Ni atomic ratio of 0.10.

The elemental analysis of Ni, Al, La and Co was carried out by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) and revealed a good accordance with the theoretical formulation.

### 2.3. Chemicals

Toluene was supplied by PANREAC (99.5% purity). Other chemicals used included commercial gases at purity >99.999%: hydrogen, nitrogen, air, helium and argon as well as standard gas mixtures (CO, $CO_2$ and nitrogen) for calibration of the CO–$CO_2$ analyzer and ($H_2$, $N_2$, CO, $CO_2$, $CH_4$ and $C_2$ gases) for the calibration of the gas chromatograph.

## 3. Results and discussion

### 3.1. Influence of catalyst composition

Table 1 presents the overall results obtained in experiments performed with the different catalysts. An experiment without catalyst is also included (run 1) as a reference to show the extent of thermal decomposition of the toluene and tube wall reactions. The table shows the values of experimental variables, such as the catalyst, catalyst weight, temperature, reaction time, S/C and $W/m_t$ ratios. Also indicated are the recovery, the carbon conversion defined as the percentage of carbon contained in the toluene converted into gases (CO, $CO_2$ and $CH_4$), the total gas yield (expressed as a mass fraction of toluene), the yields of different gases (as mass fractions of toluene) and the gas composition (expressed as molar percentages; $N_2$- and $H_2O$-free).

Steam reforming of toluene without catalyst produces very low carbon conversion to gas (3.70%) and gas yields, both increasing significantly with the presence of a catalyst. For example, with a Ni/Al catalyst 56.24% carbon conversion to gas is reached and $H_2$ and $CO_2$ yields are 0.269 and 1.010 g/g toluene, respectively.

All the catalytic experiments can be compared because they have been performed with similar $W/m_t$ and S/C ratios. The analysis of runs 2–5 shows the effect of the lanthanum content in the catalyst in toluene steam reforming. Higher carbon conversions to gas are obtained for the catalysts with La/Ni ratios of 0.044 and 0.088. These catalysts also produce higher total gas, $H_2$, $CH_4$, CO and $CO_2$ yields. The catalyst with the highest lanthanum content produces similar results to those obtained with the Ni/Al catalyst.

The analysis of runs 2, 6, 7 and 8 shows the effect of the cobalt content. The catalyst with the best performance is that with a Co/Ni ratio of 0.10. This shows the highest carbon conversion to gas, total gas yield and yields to different gases. The results of run 8 (Co/Ni = 0.25) and the Ni/Al catalyst are quite similar.

The results indicate that there exists an optimum in the amount of promoter present in Ni/Al catalysts. For Ni/Al/La catalysts it has been previously found [43] that the addition of lanthanum oxide presents some beneficial effects for methane reforming with carbon dioxide. Among the positive effects can be cited the improvement of metallic dispersion. However, there was a limit to the amount of lanthanum oxide above which metallic dispersion was not favored.

Although catalyst deactivation is not observed for the reaction times employed in the experiments of this work, other authors [37] indicate that the presence of cobalt in nickel catalysts inhibit carbon formation in carbon dioxide reforming of methane. These authors also observe that the catalyst with only cobalt presents low activity due to metal oxidation. They concluded that there is an appropriate Co/Ni ratio for an operation without metal oxidation and carbon formation.

### 3.2. Influence of S/C ratio

In order to study the influence of the S/C ratio on gas yields, several experiments have been performed using the Ni/Co/Al catalyst with a Co/Ni ratio of 0.10. The experiments have been carried out at 650 °C, using a $W/m_t$ ratio of around 7 g catalyst min/g toluene. The S/C ratio ranged from 5.5 to 1.5. The results obtained are presented in Table 2.

The results show a significant decrease in carbon conversion for a S/C ratio of 1.5 (run 11). Total gas, $H_2$ and $CO_2$ yields decrease when the S/C ratio decreases, this decrease being more pronounced for the smallest S/C ratio. The $CH_4$ yield increases when the S/C ratio diminishes. The CO yield increases for S/C ratios of 5.5–2.0 and slightly decreases for the S/C ratio of 1.5.

These gas yield evolutions with the S/C ratio can be explained by the reactions involved in toluene steam reforming. The main reactions are as follows:

Steam reforming

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \tag{1}$$

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2 \tag{2}$$

Water–gas shift

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

Dry reforming

$$C_7H_8 + 7CO_2 \rightarrow 14CO + 4H_2 \tag{4}$$

Hydrodealkylation

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \tag{5}$$

Methane steam reforming

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{6}$$

Methane steam reforming is significantly affected by the S/C ratio. When this ratio has a value of 5.5, a small amount of $CH_4$ is produced. The water–gas shift reaction produces $H_2$ and $CO_2$ at high values of S/C ratios, while at a S/C ratio of 1.5, a low $CO_2$ yield is produced and the $H_2$ yield decreases. The increase in the CO yield when the S/C ratio decreases can be explained by the water–gas shift reaction where less $H_2$ and $CO_2$ are generated and more CO is produced. At the very low S/C ratio of 1.5, toluene steam reforming and dry reforming reactions can be affected and less CO and $H_2$ are generated.

The tendencies presented in Table 2 are also observed in Figs. 3–5. In Fig. 6, the total gas yield is represented versus time. S/C ratios of 3.1 and 5.5 achieve the highest values of total gas yields. For the reaction time of the experiments of this work, deactivation of the catalyst is only appreciated for low values of S/C ratios. Thus, a decrease of $H_2$, CO, $CO_2$ and total gas yields is observed for S/C ratios of 1.5 and 2.0.

Table 3 presents a comparison of experimental gas yields with the corresponding thermodynamic equilibrium yields for the different S/C ratios. In most cases, the experimental yields are lower than the equilibrium yields. The tendencies followed by thermodynamic equilibrium yields are also similar to the experimental yields, except for CO at S/C = 1.5.

Table 1

Results of toluene steam reforming with different catalysts

| | Run 1<br>No<br><br>650 °C[b]<br>5.7 mol/mol[c] | Run 2<br>Ni/Al[a]<br><br>650 °C[b]<br>5.4 mol/mol[c] | Run 3<br>Ni/Al/La[a]<br>(La/Ni = 0.044)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 4<br>Ni/Al/La[a]<br>(La/Ni = 0.088)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 5<br>Ni/Al/La[a]<br>(La/Ni = 0.13)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 6<br>Ni/Co/Al[a]<br>(Co/Ni = 0.025)<br>650 °C[b]<br>5.5 mol/mol[c] | Run 7<br>Ni/Co/Al[a]<br>(Co/Ni = 0.10)<br>650 °C[b]<br>5.5 mol/mol[c] | Run 8<br>Ni/Co/Al[a]<br>(Co/Ni = 0.25)<br>650 °C[b]<br>6.0 mol/mol[c] |
|---|---|---|---|---|---|---|---|---|
| Catalyst weight | 0 | 1.20 | 1.20 | 1.20 | 1.20 | 1.13 | 1.20 | 1.20 |
| $W/m_t$ (g cat min/g toluene) | 0 | 6.66 | 6.63 | 6.63 | 6.63 | 6.64 | 7.05 | 7.50 |
| Reaction time (min) | 81 | 98 | 84 | 84 | 89 | 96 | 90 | 90 |
| Recovery (%) | 87.09 | 95.44 | 93.92 | 95.53 | 92.72 | 98.20 | 93.62 | 96.54 |
| Carbon conversion (%) | 3.70 | 56.24 | 78.21 | 75.05 | 57.75 | 67.25 | 71.61 | 59.78 |
| Total gas yield (g/g toluene) | 0.127 | 1.833 | 2.462 | 2.372 | 1.782 | 2.261 | 2.402 | 1.982 |
| Gas yields (g/g toluene) | | | | | | | | |
| $H_2$ | 0.004 | 0.269 | 0.311 | 0.340 | 0.249 | 0.321 | 0.342 | 0.259 |
| $CH_4$ | 0.000 | 0.002 | 0.011 | 0.015 | 0.009 | 0.002 | 0.003 | 0.003 |
| CO | 0.007 | 0.552 | 0.784 | 0.795 | 0.673 | 0.539 | 0.581 | 0.478 |
| $CO_2$ | 0.113 | 1.010 | 1.356 | 1.222 | 0.851 | 1.399 | 1.476 | 1.242 |
| Gas composition (%mol, $N_2$- and $H_2O$-free) | | | | | | | | |
| $H_2$ | 55.4 | 75.9 | 72.3 | 74.9 | 73.9 | 75.8 | 75.8 | 74.0 |
| $CH_4$ | 0.0 | 0.1 | 0.3 | 0.4 | 0.3 | 0.1 | 0.1 | 0.1 |
| CO | 4.0 | 11.1 | 13.0 | 12.5 | 14.3 | 9.1 | 9.2 | 9.8 |
| $CO_2$ | 40.6 | 12.9 | 14.3 | 12.2 | 11.5 | 15.0 | 14.9 | 16.1 |

[a] Catalyst.

[b] Temperature.

[c] S/C ratio.

Table 2
Results of toluene steam reforming with Ni/Co/Al (Co/Ni = 0.10) catalyst

| | Run 7<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>5.5 mol/mol[c] | Run 9<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>3.1 mol/mol[c] | Run 10<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>2.0 mol/mol[c] | Run 11<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>1.5 mol/mol[c] |
|---|---|---|---|---|
| Catalyst weight | 1.20 | 2.32 | 3.04 | 4.32 |
| $W/m_t$ (g cat min/g toluene) | 7.05 | 7.48 | 6.75 | 7.20 |
| Reaction time (min) | 90 | 90 | 90 | 90 |
| Recovery (%) | 93.62 | 94.03 | 91.70 | 96.79 |
| Carbon conversion (%) | 71.61 | 72.84 | 70.25 | 54.12 |
| Total gas yield (g/g toluene) | 2.402 | 2.367 | 2.155 | 1.535 |
| Gas yields (g/g toluene) | | | | |
| $H_2$ | 0.342 | 0.310 | 0.265 | 0.176 |
| $CH_4$ | 0.003 | 0.011 | 0.015 | 0.019 |
| CO | 0.581 | 0.634 | 0.764 | 0.734 |
| $CO_2$ | 1.476 | 1.412 | 1.110 | 0.606 |
| Gas composition (%mol, $N_2$- and $H_2O$-free) | | | | |
| $H_2$ | 75.8 | 73.7 | 71.3 | 68.1 |
| $CH_4$ | 0.1 | 0.3 | 0.5 | 0.9 |
| CO | 9.2 | 10.8 | 14.7 | 20.3 |
| $CO_2$ | 14.9 | 15.3 | 13.6 | 10.7 |

Influence of S/C ratio.

[a] Catalyst.

[b] Temperature.

[c] S/C ratio.

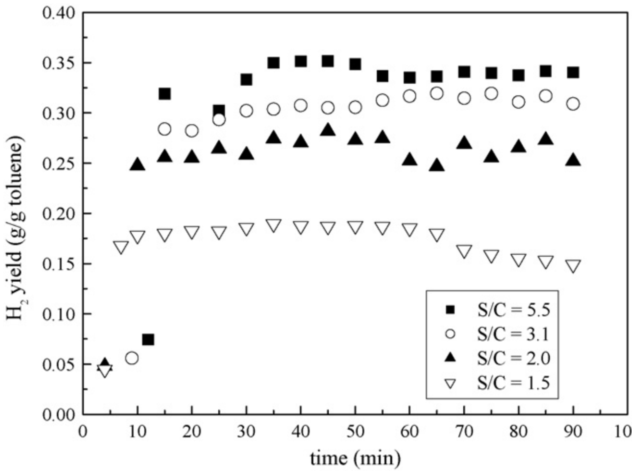

Fig. 3. $H_2$ yield evolution with time, influence of S/C ratio (Co/Ni = 0.10 catalyst).

Table 3
Comparison of experimental gas yields with the corresponding thermodynamic equilibrium yields

| Gas | S/C = 5.5 | | S/C = 3.1 | | S/C = 2.0 | | S/C = 1.5 | |
|---|---|---|---|---|---|---|---|---|
| | Exp. | Equi. | Exp. | Equi. | Exp. | Equi. | Exp. | Equi. |
| $H_2$ | 0.342 | 0.356 | 0.310 | 0.322 | 0.265 | 0.278 | 0.176 | 0.236 |
| $CH_4$ | 0.003 | 0.002 | 0.011 | 0.016 | 0.015 | 0.061 | 0.019 | 0.124 |
| CO | 0.581 | 0.487 | 0.634 | 0.851 | 0.764 | 1.159 | 0.734 | 1.303 |
| $CO_2$ | 1.476 | 2.581 | 1.412 | 1.964 | 1.110 | 1.362 | 0.606 | 0.959 |

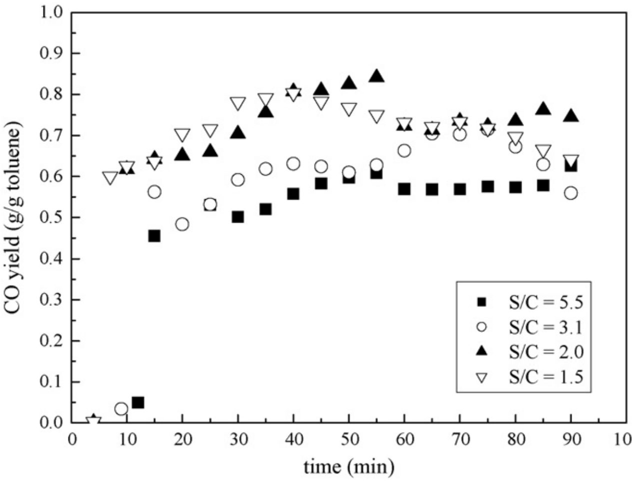

Fig. 4. CO yield evolution with time, influence of S/C ratio (Co/Ni = 0.10 catalyst).

### 3.3. Influence of $W/m_t$ ratio

With the purpose of analyzing the influence of the $W/m_t$ ratio on the gas yields, Tables 4 and 5 present the results obtained with Ni/Al/La catalyst with a La/Ni ratio of 0.088 and Ni/Co/Al catalyst with Co/Ni = 0.10, respectively. A S/C ratio of around 5.5 has been selected.

The general tendency shown in Tables 4 and 5 is that carbon conversion and total gas yields increase when the $W/m_t$ ratio increases, as do the $H_2$ and $CO_2$ yields. The $CH_4$ and CO yields do not show a clear tendency, except for the CO yield with Ni/Co/Al (Co/Ni = 0.10) catalyst that slightly increases when the $W/m_t$ ratio increases.

Table 4
Results of toluene steam reforming with Ni/Al/La catalyst (La/Ni = 0.088)

| | Run 12<br>Ni/Al/La[a] (La/Ni = 0.088)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 4<br>Ni/Al/La[a] (La/Ni = 0.088)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 13<br>Ni/Al/La[a] (La/Ni = 0.088)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 14<br>Ni/Al/La[a] (La/Ni = 0.088)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 15<br>Ni/Al/La[a] (La/Ni = 0.088)<br>650 °C[b]<br>5.7 mol/mol[c] | Run 16<br>Ni/Al/La[a] (La/Ni = 0.088)<br>650 °C[b]<br>5.7 mol/mol[c] |
|---|---|---|---|---|---|---|
| Catalyst weight | 0.9 | 1.20 | 1.60 | 2.00 | 3.00 | 4.00 |
| $W/m_t$ (g cat min/g toluene) | 4.97 | 6.63 | 8.84 | 11.05 | 16.57 | 22.10 |
| Reaction time (min) | 81 | 84 | 81 | 79 | 79 | 81 |
| Recovery (%) | 97.07 | 95.53 | 95.67 | 97.12 | 94.48 | 99.11 |
| Carbon conversion (%) | 64.28 | 75.05 | 84.01 | 82.28 | 92.96 | 94.53 |
| Total gas yield (g/g toluene) | 2.059 | 2.372 | 2.761 | 2.777 | 3.115 | 3.156 |
| Gas yields (g/g toluene) | | | | | | |
| $H_2$ | 0.305 | 0.340 | 0.360 | 0.377 | 0.394 | 0.426 |
| $CH_4$ | 0.008 | 0.015 | 0.006 | 0.010 | 0.009 | 0.011 |
| CO | 0.672 | 0.795 | 0.702 | 0.590 | 0.657 | 0.727 |
| $CO_2$ | 1.074 | 1.222 | 1.693 | 1.800 | 2.055 | 1.992 |
| Gas composition (%mol, $N_2$- and $H_2O$-free) | | | | | | |
| $H_2$ | 75.7 | 74.9 | 73.8 | 75.1 | 73.6 | 74.8 |
| $CH_4$ | 0.2 | 0.4 | 0.2 | 0.2 | 0.2 | 0.2 |
| CO | 11.9 | 12.5 | 10.3 | 8.4 | 8.8 | 9.1 |
| $CO_2$ | 12.1 | 12.2 | 15.8 | 16.3 | 17.4 | 15.9 |

Influence of $W/m_t$ ratio.

[a] Catalyst.

[b] Temperature.

[c] S/C ratio.

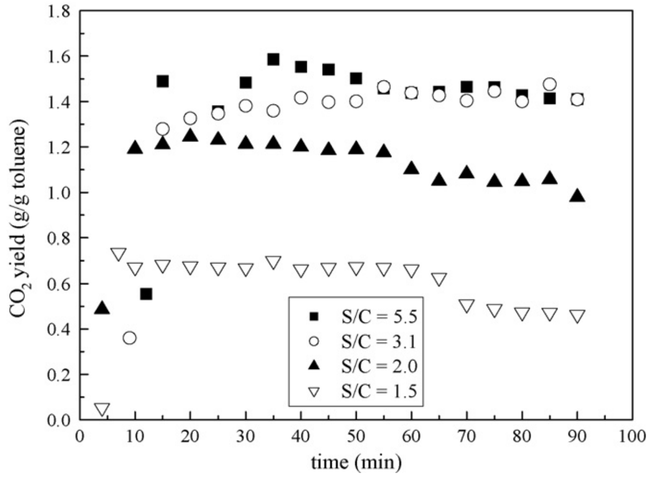

Fig. 5. $CO_2$ yield evolution with time, influence of S/C ratio (Co/Ni = 0.10 catalyst).

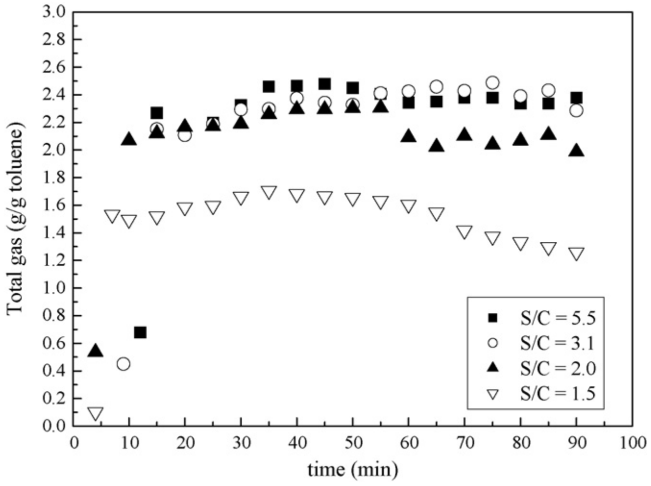

Fig. 6. Total gas yield evolution with time, influence of S/C ratio (Co/Ni = 0.10 catalyst).

Hydrodealkylation reaction [29] and also the inverse of methane steam reforming can explain the formation of $CH_4$. The increase of $H_2$ and $CO_2$ yields when the $W/m_t$ ratio increases can be due to the participation of the catalyst in the water–gas shift reaction.

A comparison of experimental gas yields with those corresponding to thermodynamic equilibrium ($H_2 = 0.356$ g/g toluene; $CH_4 = 0.002$ g/g toluene; $CO = 0.487$ g/g toluene and $CO_2 = 2.581$ g/g toluene) shows that the $H_2$ yield reaches the values of equilibrium while $CO_2$ yields tend towards equilibrium value when the $W/m_t$ ratio increases. Some of the values of the $H_2$ yield are higher than the equilibrium yield, but these are considered to be an experimental error. The $CH_4$ and CO yields are higher than the equilibrium values for the majority of the $W/m_t$ ratios studied.

With respect to the gas composition, from Tables 4 and 5 it is observed that $H_2$ and $CH_4$ contents are quite similar for the different $W/m_t$ ratios studied. The CO content tends to decrease when the $W/m_t$ ratio increases, while the $CO_2$ content tends to increase.

In order to compare the results obtained with the Ni/Al/La catalyst (La/Ni = 0.088) and the Co/Ni/Al catalyst (Co/Ni = 0.10), Tables 4 and 5 can be analyzed for a similar $W/m_t$ ratio. For a given $W/m_t$ ratio, the $H_2$ yield is similar for the two catalysts. For low $W/m_t$ ratios (smaller than 11.05 g catalyst min/g toluene) the CO yields are higher for the Ni/Al/La catalyst. When the $W/m_t$

Table 5
Results of toluene steam reforming with Ni/Co/Al (Co/Ni = 0.10) catalyst

| | Run 17<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>5.9 mol/mol[c] | Run 7<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>5.5 mol/mol[c] | Run 18<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>5.4 mol/mol[c] | Run 19<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>6.2 mol/mol[c] | Run 20<br>Ni/Co/Al[a] (Co/Ni = 0.1)<br>650 °C[b]<br>6.2 mol/mol[c] |
|---|---|---|---|---|---|
| Catalyst weight | 0.80 | 1.20 | 1.60 | 2.00 | 2.40 |
| $W/m_t$ (g cat min/g toluene) | 4.70 | 7.05 | 8.88 | 12.50 | 15.00 |
| Reaction time (min) | 90 | 90 | 90 | 90 | 90 |
| Recovery (%) | 98.08 | 93.62 | 93.87 | 95.81 | 97.41 |
| Carbon conversion (%) | 69.48 | 71.61 | 74.22 | 87.04 | 89.85 |
| Total gas yield (g/g toluene) | 2.308 | 2.402 | 2.515 | 2.933 | 3.001 |
| Gas yields (g/g toluene) | | | | | |
| $H_2$ | 0.311 | 0.342 | 0.363 | 0.373 | 0.386 |
| $CH_4$ | 0 | 0.003 | 0.002 | 0.004 | 0.014 |
| CO | 0.576 | 0.581 | 0.576 | 0.607 | 0.645 |
| $CO_2$ | 1.421 | 1.476 | 1.574 | 1.949 | 1.956 |
| Gas composition (%mol, $N_2$- and $H_2O$-free) | | | | | |
| $H_2$ | 74.6 | 75.8 | 76.3 | 73.8 | 73.8 |
| $CH_4$ | 0 | 0.1 | 0.1 | 0.1 | 0.3 |
| CO | 9.9 | 9.2 | 8.6 | 8.6 | 8.8 |
| $CO_2$ | 15.5 | 14.9 | 15.0 | 17.5 | 17.0 |

Influence of $W/m_t$ ratio.

[a] Catalyst.

[b] Temperature.

[c] S/C ratio.

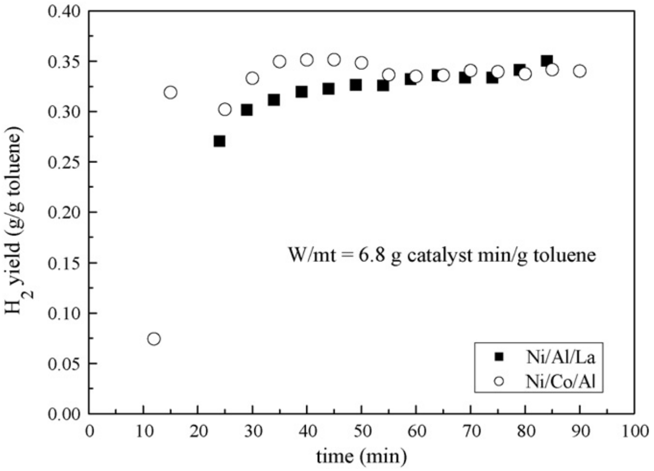

Fig. 7. $H_2$ yield evolution with time, influence of catalyst composition (La/Ni = 0.088 and Co/Ni = 0.10).

ratio increases, gas yields are more similar for the two catalysts. As an example, Figs. 7–9 present $H_2$, CO and $CO_2$ yields, respectively, for a $W/m_t$ ratio of around 6.8 g catalyst min/g toluene. As a main conclusion it can be deduced that Ni/Co/Al catalyst with Co/Ni = 0.10 and Ni/Al/La catalyst with La/Ni = 0.088 show a similar degree of activity in toluene steam reforming.

A simple kinetic study has been performed using the results of the catalytic steam reforming of toluene with Ni/Al/La (La/Ni = 0.088) and Ni/Co/Al (Co/Ni = 0.10) catalysts, using different $W/m_t$ ratios.

In non-catalytic toluene steam reforming almost no conversion of toluene occurs, demonstrating that the catalyst plays a significant role in gas formation and that the catalytic step is the main step. $H_2$ and $CO_2$ are product gases in the catalytic step given that their yields increase with the $W/m_t$ ratio. $CH_4$ and CO are also product gases in the catalytic step, but they do not show a clear tendency. $CH_4$ may be a product gas of toluene hydrodealkylation [29] and a reactive gas of methane steam reforming. CO may be a product gas of toluene steam reforming and dry reforming and a reactive gas of the water–gas shift reaction. Because the $H_2$ yields are close to the thermodynamic equilibrium yield, only $CO_2$ is considered in the kinetic study.

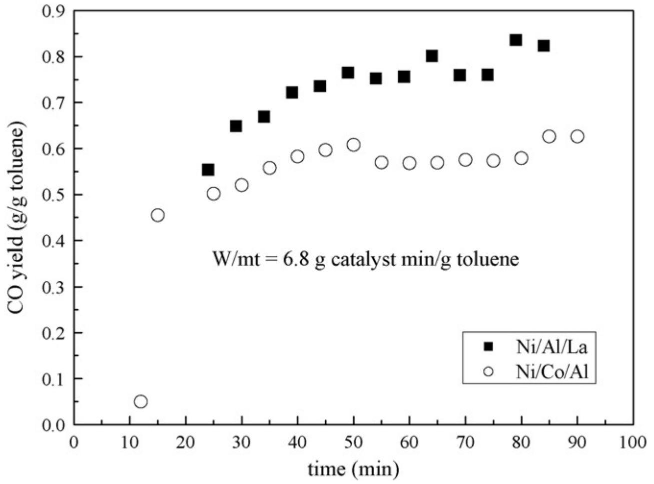

Fig. 8. CO yield evolution with time, influence of catalyst composition (La/Ni = 0.088 and Co/Ni = 0.10).

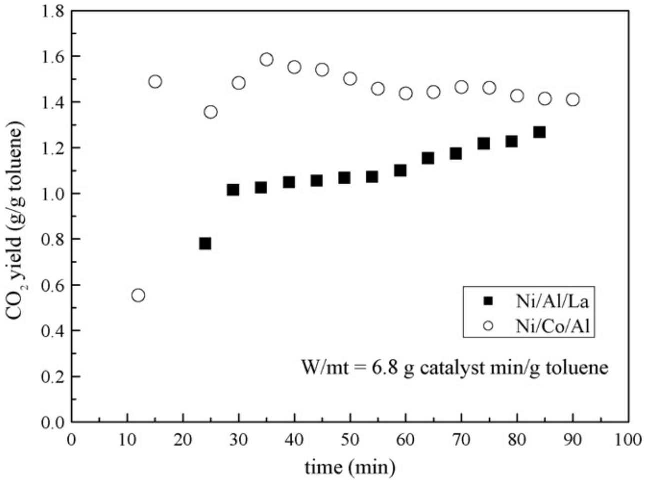

Fig. 9. $CO_2$ yield evolution with time, influence of catalyst composition (La/Ni = 0.088 and Co/Ni = 0.10).

Applying a mass balance for $CO_2$ in a differential element of catalyst weight and assuming a plug flow of gases, the following equation is obtained:

$$\mathrm{d}m_{CO_2} = r_{CO_2}\,\mathrm{d}W \tag{7}$$

where $r_{CO_2}$ (given in units of g $CO_2$/g catalyst min) is the formation rate for $CO_2$, and $m_{CO_2}$ (given in units of g/min) is the flow rate of $CO_2$ in the catalytic step.

From Eq. (7), it is obtained that

$$r_{CO_2} = \frac{\mathrm{d}m_{CO_2}}{\mathrm{d}W} \tag{8}$$

Eq. (8) is transformed by dividing both terms by the flow rate of the inlet toluene:

$$r_{CO_2} = \frac{\mathrm{d}(m_{CO_2}/m_t)}{\mathrm{d}(W/m_t)} \tag{9}$$

A first-order kinetic equation is proposed, where the reaction rate is determined by multiplying the kinetic constant by a driving force. The driving force used is the difference between the maximum yield of a specific gas and the experimental yield obtained. The maximum yield would correspond to the values of thermodynamic equilibrium. The equation is

$$r_{CO_2} = k_{CO_2}\left[\left(\frac{m_{CO_2}}{m_t}\right)_{\mathrm{equ}} - \left(\frac{m_{CO_2}}{m_t}\right)\right] \tag{10}$$

where $k_{CO_2}$ is the kinetic coefficient for the formation of $CO_2$ (given in units of g toluene/g catalyst min) and $(m_{CO_2}/m_t)_{\mathrm{equ}}$ is the yield of $CO_2$ in the thermodynamic equilibrium.

Applying Eq. (9), the gas formation rates of $CO_2$ can be obtained from the experimental data of $m_{CO_2}/m_t$ versus $W/m_t$ by derivation. These reaction rates have been represented versus the driving force. Fig. 10 shows the procedure to obtain the kinetic constant for the two catalysts. The kinetic

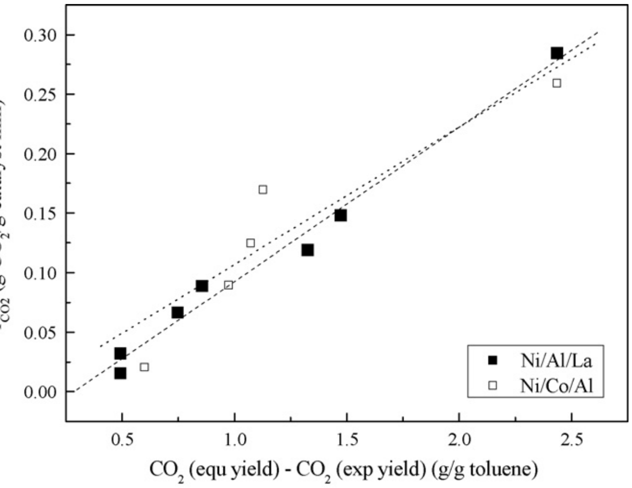

Fig. 10. Procedure to obtain the kinetic constant of $CO_2$.

constant is 0.1296 g toluene/g catalyst min for the Ni/Al/La catalyst (La/Ni = 0.088) and 0.1187 g toluene/g catalyst min for the Ni/Co/Al catalyst (Co/Ni = 0.10) with regression coefficients $R$ of 0.9924 and 0.9296, respectively.

## 4. Conclusions

Toluene steam reforming has been studied in a fluidized bed reactor at 650 °C using coprecipitated Ni/Al catalysts promoted with lanthanum or cobalt. The main conclusions obtained are as follows:

(1) The catalyst plays a significant role in toluene steam reforming, increasing significantly carbon conversion and yields to different gases.
(2) The content of the promoter in the catalyst composition significantly influences its performance. The order of activity for Ni/Al/La catalysts is: La/Ni = 0.13 ≈ La/Ni = 0 < La/Ni = 0.088 ≈ La/Ni = 0.044. For Ni/Co/Al catalysts it is: Co/Ni = 0 ≈ Co/Ni = 0.25 < Co/Ni = 0.025 < Co/Ni = 0.10.
(3) The influence of the S/C ratio on gas yields has been studied using the Ni/Co/Al catalyst with a Co/Ni ratio of 0.10. $H_2$ and $CO_2$ yields decrease, while $CH_4$ and CO yields increase when the S/C ratio diminishes from 5.5 to 1.5. These effects are more pronounced for the smallest S/C ratio studied.
(4) The $W/m_t$ ratio significantly influences gas yields. When the $W/m_t$ ratio increases, $H_2$ and $CO_2$ yields increase, as do the carbon conversion and total gas yield, for the two selected catalysts: Ni/Al/La with La/Ni = 0.088 and Ni/Co/Al with Co/Ni = 0.10.
(5) A first-order kinetic equation has been proposed for the formation of $CO_2$.

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