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# 1 Evolution of dolomite composition and reactivity during biomass 2 gasification

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## 11 Abstract

12 Dolomite is a cheap and robust catalyst used for biomass gasification, but its deactivation under  
13 relevant conditions of pilot-scale gasifiers has still been poorly understood. For this reason, the  
14 catalytic activity of fresh and used dolomites produced from an industrial air-blow fluidized bed  
15 was investigated. Fresh and used dolomites were characterized by BET, SEM-EDX, XPS, ICP-  
16 MS, XRD, TPD and TPO. Benzene steam reforming was selected as a surrogate reaction of tar  
17 conversion in order to probe the reactivity of the two dolomites. The activity of used dolomite  
18 was 25% lower than that of fresh dolomite. This difference could be explained by: (1) the  
19 deposition of a Si-based layer from biomass ashes at the surface of used dolomite, and (2) the  
20 production of coke during gasification. The reaction mechanism of benzene steam reforming  
21 over fresh and used dolomites was discussed. For used dolomite, the Si and coke depositions  
22 reduced the availability of the active sites (CaO, MgO) thus lowering the conversion of benzene.  
23 These deposits could also inhibit the interactions between CaO and MgO and enhance the  
24 formation of a stable coke.

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**Keywords**

biomass; dolomite; gasification; syngas; tar; up-grading.

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## 47 1. Introduction

48 Renewable alternative routes for energy production appear as an important challenge to  
49 reduce the greenhouse gases emissions while meeting the growing world energy demand.  
50 Biomass gasification is an attractive way to convert a renewable resource into several energy  
51 carriers, such as substitute natural gas, bio-hydrogen, or Fischer-Tropsch biofuel [1].  
52 Nevertheless, the removal of the syngas pollutants (such as tars) is required before further  
53 valorization, and this step remains the major issue in the development of gasification processes.  
54 Tar is formed by pyrolysis reactions combined with incomplete oxidation reactions in gasifiers  
55 [2–4] and is the most problematic pollutant contained in the syngas [2]. Tar is composed of a  
56 wide variety of aromatic and oxygenated compounds classified in different classes depending on  
57 their properties [5] or their thermal history (primary, secondary and tertiary tar) [2]. These  
58 compounds can condense along the process chain thus impeding syngas valorization. The  
59 concentration of tar must be drastically reduced in order to meet the standards required for  
60 syngas ranging from about 50 mg/Nm<sup>3</sup> (or a dew point lower than 35°C for engine [6]) to 0.1  
61 mg/Nm<sup>3</sup> (for Fischer-Tropsch synthesis) [7]. In addition, tar in syngas considerably reduces the  
62 cold gas efficiency of gasifiers. Indeed, benzene can represent 0.5% of biomass LHV in air dense  
63 fluidized bed gasifier [3].

64 For these reasons, the catalytic conversion of tar into gaseous products (CO, H<sub>2</sub>, CH<sub>4</sub>) is  
65 of tremendous importance for improving the gasification processes. The main drawbacks of the  
66 catalytic methods are the cost of the catalysts and their deactivation. This topic has been  
67 intensively studied over the past 30 years, and several reviews have reported the main conclusions  
68 [8–20]. These studies focused on the conversion of real biomass tars, or tar surrogate molecules.  
69 Benzene, toluene and naphthalene are often considered as surrogate tar compounds due to their  
70 significant concentration in syngas and to their stability [9,21,22]. Benzene is the most important  
71 aromatic compound present in the syngas and the most stable one [22–24]. For this reason it is a  
72 good surrogate of tertiary (high temperature) tar.

73 A large variety of catalysts were tested for tar decomposition: chars [25–28], zeolites  
74 [29,30], iron oxides [31], noble metals [32–37], alkaline and alkaline earth metals (AAEM) [38,39],  
75 nickel catalysts [40,41], clay minerals [13], olivine [42,43], and calcined rocks (magnesite, calcite,  
76 dolomite) [44–46]. Carbonate rocks, such as dolomite, were identified as promising catalysts due  
77 their abundance and low-cost [47–51].

78 Dolomite is a natural magnesium ore (MgCO<sub>3</sub>.CaCO<sub>3</sub>) composed of a mixture of calcium  
79 carbonate and magnesium carbonate at a concentration ratio of nearly 1:1. A tremendous number  
80 of articles highlighted that dolomite is an active catalyst for tar removal [48,52–64]. A calcination

81 step is required to increase the catalytic activity of dolomite by eliminating CO<sub>2</sub> and transforming  
82 (CaMg(CO<sub>3</sub>)<sub>2</sub>) into active CaO and MgO [65]. CaO is known to be more active than MgO in tar  
83 cracking reactions and is mainly responsible for the high activity of calcined dolomite [66].  
84 However, a synergistic interaction between CaO and MgO plays an important role in the activity  
85 of dolomite. Indeed, catalysts based on mechanical mixtures of MgO and CaO have presented a  
86 better performance than CaO alone [67]. In addition, dolomite was proved to be more active  
87 than magnesite (MgCO<sub>3</sub>) and calcite (CaCO<sub>3</sub>) for tar reforming [50,64]. The higher activity of  
88 dolomite is mainly explained by the lower deactivation by coke deposition, as a result of the  
89 presence of MgO which inhibits the formation of stable carbonaceous materials at the surface of  
90 CaO, and which promotes the formation of less stable carbon species that are easily gasified [68].  
91 Therefore, the deactivation of CaO active sites by coke deposition is reduced. The presence of  
92 iron in dolomites is also expected to play a role in the steam reforming of tar as well as in the  
93 water-gas shift reaction [56,64].

94 Some articles specifically studied the decomposition of benzene [52,54], toluene [69–71]  
95 and naphthalene [53,72] over calcined dolomite. The tests were conducted at 700-900 °C under  
96 different atmospheres: steam, carbon dioxide or syngas mixtures. The benzene decomposition  
97 reactions mainly generated H<sub>2</sub> and CO<sub>2</sub>, while CO was a minor product and was generated in  
98 lower amount with rising temperature. These reactions were inhibited by hydrogen which may be  
99 dissociatively adsorbed on the metal-oxide adsorption sites, thus preventing the tar access to  
100 adsorption sites [73,74]. The CO<sub>2</sub> concentration in the syngas and the temperature strongly  
101 influence the activity of dolomite. Indeed, the dolomite can be carbonated (depending on the  
102 thermodynamic equilibrium of CO<sub>2</sub>/CaO/CaCO<sub>3</sub>) which results in the decrease of its catalytic  
103 activity for tar cracking [47,55]. Dolomite can be deactivated by hydration and carbonation  
104 reactions [75].

105 Syngas cleaning processes are classified in two types depending on their location; either in  
106 the gasifier (primary methods) or downstream of the gasifier (secondary methods) [77].  
107 Secondary methods may be slightly more efficient than primary ones but a specific catalytic  
108 cracking reactor is required thus increasing the investment and operating costs of the gasification  
109 unit. Dolomite as in-bed material was shown to be an efficient catalyst for tar cracking [49]  
110 allowing the production of a relatively clean syngas. For this reason, dolomite is often used as bed  
111 material in gasification and notably in many recent studies [78–81].

112

113 In fluidized bed gasifier, dolomite is in contact with biomass particles, and a modification  
114 of its surface properties is likely to occur. These modifications could change the long-term

115 catalytic activity of “used dolomite” for tar cracking, thus modifying the syngas yield and quality.  
116 This crucial topic has never yet been explored for dolomite whereas it has been extensively  
117 studied for olivine. Indeed, several studies showed that olivine is coated by ash materials during  
118 biomass gasification and this ash layer considerably increases the reactivity of olivine for tar  
119 cracking and WGS reactions [82–88]. This present work reveals that the impact of ashes may be  
120 very different for dolomite than for olivine.

121 To the best of our knowledge, this work presents for the first time the effect of dolomite  
122 aging under significant gasification conditions (in a pilot plant) on tar conversion. Dolomites  
123 before and after gasification of biomass were characterized by complementary methods (BET,  
124 SEM-EDX, XRD, XPS, TPO, TPD). Then the reactivity of these 2 dolomites (pristine and used)  
125 was studied by a “probe” key reaction of tar conversion which is the steam reforming of  
126 benzene. Finally the mechanisms of benzene steam reforming over dolomites are discussed.

## 127 **2. Materials & Methods**

### 128 **2.1. Presentation of the dolomite samples**

129 The dolomite originating from Cantabria (Spain) was calcined at 1000°C for few hours  
130 before being used as a catalyst in a biomass gasification plant at Portalegre, Portugal (EQTEC  
131 technology) [89]. The gasification reactor was a dense fluidized bed operated at a temperature of  
132 750°C for 10 days using air as gasifying agent. Biomass was a mixture of wood (70%) and  
133 miscanthus (30%) and was fed in the reactor at a flow-rate of 50kg/h. The analysis of biomass is  
134 presented in supplementary material. The dolomite samples were denoted as “fresh” after  
135 calcination, and “used” after gasification. Both samples were sieved to particle sizes from 100 to  
136 250µm.

### 137 **2.2. Characterizations of the catalysts**

138 The morphology of fresh and used dolomite materials was studied on a scanning electron  
139 microscope (SEM) JEOL model JSM-6490LV combined with energy dispersive X-ray  
140 spectroscopy (EDX) to analyse the chemical composition of the surface.

141 For inductively coupled plasma mass spectrometry (ICP-MS) analysis of the bulk, the  
142 samples were dissolved in lithium metaborate (LiBO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>) solutions following  
143 the CNRS-SARM procedure [90].

144 The crystalline structure of the fresh and used dolomites was analysed by X-ray  
145 diffraction (XRD) measurements. XRD analyses were performed at room temperature using a  
146 Philips Panalytical X’Pert Pro MPD diffractometer equipped with Xcelerator detector. XRD

147 patterns were collected with a  $\text{CuK}\alpha$  radiation source operating at 40kV and 40mA. The  
148 diffraction pattern was collected in the range  $2\theta = 10\text{-}80^\circ$ , with a step size of  $0.016^\circ$  in  $2\theta$ , and a  
149 scan speed of  $1.7\text{min}^{-1}$ .

150 XPS analyses were performed using a KRATOS Axis Ultra X-ray photoelectron  
151 spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromatic Al  $\text{K}\alpha$  X-ray  
152 source ( $h\nu=1486.6\text{eV}$ ) operated at 150W. Spectra were collected at normal ( $90^\circ$ ) take-off angle  
153 and the analysis area was  $700\times 300\mu\text{m}$ . The base pressure in the analytical chamber was  $10^{-9}\text{mbar}$   
154 during XPS measurements. Wide scans were recorded using an analyser pass energy of 160eV,  
155 while narrow scans were obtained using a pass energy of 20eV (instrumental resolution better  
156 than 0.5eV).

157 BET areas were determined by the one-point method using adsorbed nitrogen at 77K in a  
158 Micromeritics TriStart II instrument. The solids were previously degassed under vacuum at room  
159 temperature overnight.

160 Temperature Programmed Desorption (TPD) and Temperature Programmed Oxidation  
161 (TPO) were performed by heating the dolomite samples at  $850^\circ\text{C}$  under a  $30\text{NmL}/\text{min}$  flow of  
162 pure nitrogen (TPD) or air (TPO). A 2.5g dolomite sample was placed in a quartz U-reactor  
163 (internal diameter= $10\text{mm}$ ) heated by an electrical furnace at  $5^\circ\text{C}/\text{min}$  to  $850^\circ\text{C}$ . The exhaust gas  
164 was analysed online by a micro-gas chromatograph ( $\mu\text{GC}$ ) (SRA Instrumentation R3000).

### 165 **2.3. Catalytic experiments**

166 The experiment set-up has been presented previously [91]. Catalytic experiments were  
167 conducted on a fixed bed quartz reactor (internal diameter  $10\text{mm}$ ) placed in an electric oven. The  
168 catalytic bed was supported by a quartz sintered plate. A thermocouple was positioned within the  
169 bed of dolomite. The inlet gas composition was controlled by mass flow controllers  
170 (Bronkhorst). Benzene (supplied by Fluka, 99.9% purity) and demineralised water were added in  
171 the gas mixture by two syringe pumps and vaporised in a vaporisation chamber, swept by  
172 nitrogen and connected through a heated line to the catalytic bed. At the outlet of the catalytic  
173 bed, permanent gases were analysed on-line with a  $\mu\text{-GC}$  Varian 490 equipped with 4 modules.  
174 The outlet was also connected to a heated sampling line and to a heated sampling loop for on-  
175 line analysis of benzene by a GC/FID.

176 The operating conditions of the catalytic tests were chosen in order to obtain a contact  
177 time similar to the one used in the industrial gasification fluidized bed of EQTEC. The mass of  
178 catalyst was 3.0g and the total gas flow rate was set at  $45\text{NmL}/\text{min}$ . These conditions were set to  
179 be consistent with the industrial fluidized bed conditions (mass of fluidized dolomite bed and  
180 total outlet syngas flow rate). The benzene inlet concentration was 0.5vol% which corresponds to

181 the content usually measured in the syngas [3]. Catalytic tests were performed at 800, 850 and  
 182 900°C without applying pre-treatment to the materials. The conversion of benzene was constant  
 183 over time on stream and the value presented is an average of several points (GC/FID analysis)  
 184 over more than 50 minutes.

185 The benzene conversion ( $X_B$ ) was calculated according to Eq.1, where  $\dot{n}_B^{in}$  is the molar  
 186 flow rate of benzene feeding the reactor, and  $\dot{n}_B^{out}$  the molar flow rate of benzene leaving the  
 187 reactor.

$$188 \quad X_B = \frac{\dot{n}_B^{in} - \dot{n}_B^{out}}{\dot{n}_B^{in}} \cdot 100 \quad \text{Eq.1}$$

189 The selectivity ( $S_i$ ) of the reaction products (i) was also calculated according to Eq.2:

$$190 \quad S_i = \frac{\dot{n}_i^{out}}{\dot{n}_B^{in} - \dot{n}_B^{out}} \cdot 100 \quad \text{Eq.2}$$

191

## 192 3. Results and discussion

### 193 3.1. Characterization of the catalysts

#### 194 3.1.1. Morphology of particles and chemical composition of the bulk catalysts by ICP

195

196 Table 1 compares the values of BET surface area of fresh and used dolomite samples.  
 197 For fresh dolomite, the measured values were not high enough to be accurate. Both types of  
 198 catalysts exhibited low BET surface areas ( $< 20\text{m}^2/\text{g}$ ). However, a slight increase of the BET  
 199 surface area was observed for used dolomite samples.

200 Table 1. BET surface area of dolomite and olivine.

Catalyst	BET ( $\text{m}^2/\text{g}$ )
Fresh dolomite	0.4
Used dolomite	19.5

201 SEM images and EDX analyses of dolomite materials are presented in Figure 1 and Table 2.  
 202 EDX analysis was averaged on various particles. Dolomite is a natural material and presents an  
 203 average composition of about 17% Mg and 34% Ca. After its use as a bed material in the  
 204 fluidised bed reactor, the surface of used dolomite is enriched by inorganic elements initially  
 205 contained in the biomass. The surface of dolomite particles is coated by a layer of ashes and  
 206 becomes smoother as shown on Figure 1. The mechanisms of coating are out of the scope of the  
 207 present study and have been previously studied in details [3,92,93]. The coating behaviour



208 depends on gasification conditions and on the composition of the bed, the reactor walls and the  
 209 ashes of biomass.

210 Si and P are not detected on fresh dolomite, but their concentrations at the surface of used  
 211 dolomite are of about 2.5 and 3.7wt.% respectively (Table 2). SEM-EDX is only a first qualitative  
 212 approach of dolomites chemistry. For this reason, ICP-MS, XRD, XPS and TPD/TPO analyses  
 213 were performed in order to study more deeply the chemical composition of the catalysts.

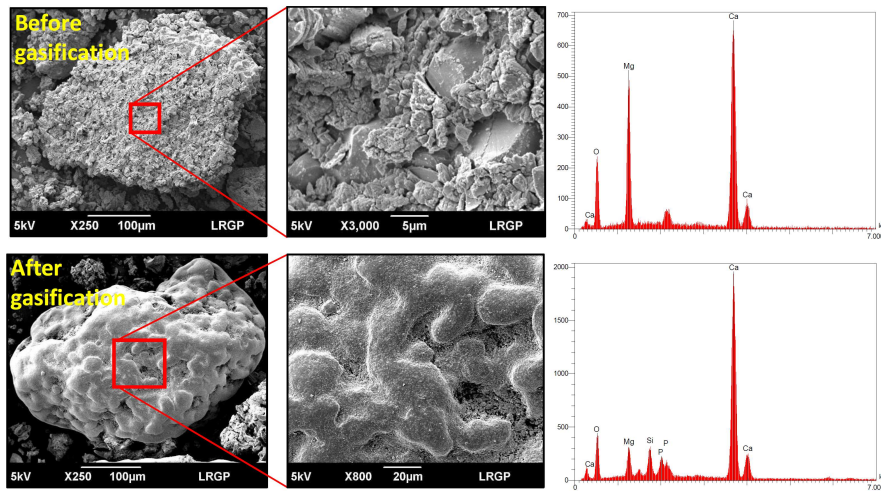
214

215

Table 2. SEM-EDX analysis of fresh and used dolomite

Elements (wt.%)	Fresh dolomite			Used dolomite		
	Min	Average	Max	Min	Average	Max
O	44.7	<b>49.4</b>	59.8	41.1	<b>48.1</b>	54.8
Mg	1.6	<b>17.0</b>	36.2	3.6	<b>5.3</b>	7.5
Ca	19.1	<b>33.7</b>	48.5	37.0	<b>41.9</b>	46.6
P	<i>nd</i>	<i>nd</i>	<i>nd</i>	2.2	<b>2.5</b>	2.7
Si	<i>nd</i>	<i>nd</i>	<i>nd</i>	3.3	<b>3.7</b>	4.1

216



217

218 Figure 1. SEM-EDX analysis of the 2 dolomites (before and after biomass gasification in a pilot  
 219 scale gasifier). SEM-EDX highlights the modification of the surface of particles which are coated  
 220 by a layer of ashes during biomass gasification.

221

222 Table 3 presents the bulk chemical composition of the catalysts analyzed by ICP-MS.  
 223 These results confirm that used catalysts were enriched in inorganic species during the biomass  
 224 gasification. Fresh dolomite is mainly composed of CaO (50%) and MgO (38%), with some  
 225 traces of iron, silicium and aluminium (presented as oxides due to the ICP analysis). After  
 226 gasification, used dolomite is mainly enriched in SiO<sub>2</sub> (4.3 wt.%, which is similar to EDX analysis)

227 and P<sub>2</sub>O<sub>5</sub> (0.39 wt.%, which is lower than EDX analysis). The two main species, CaO and MgO,  
 228 were found to decrease mainly due to the increase of SiO<sub>2</sub>, while Al<sub>2</sub>O<sub>3</sub> (1.02 wt.%) slightly  
 229 increased in used dolomite. The loss on ignition increased for used dolomite (from 9.01 to  
 230 11.88wt.%) as a result of coke deposit and carbonates. Other species present in biomass ashes  
 231 (K, Mn, etc.) are also present in higher amount in the used dolomite which is in agreement with  
 232 ash composition of biomass (presented in supplementary material). Ash composition depends on  
 233 biomass type and culture mode but these elements are often found as the main inorganic  
 234 elements of many ligno-cellulosic biomasses. Therefore this ash coating is representative and  
 235 significant for the gasification of various biomasses in air-dense fluidized bed.

236

237 **Table 3. Elemental composition of fresh and used dolomite (obtained by ICP-MS).**

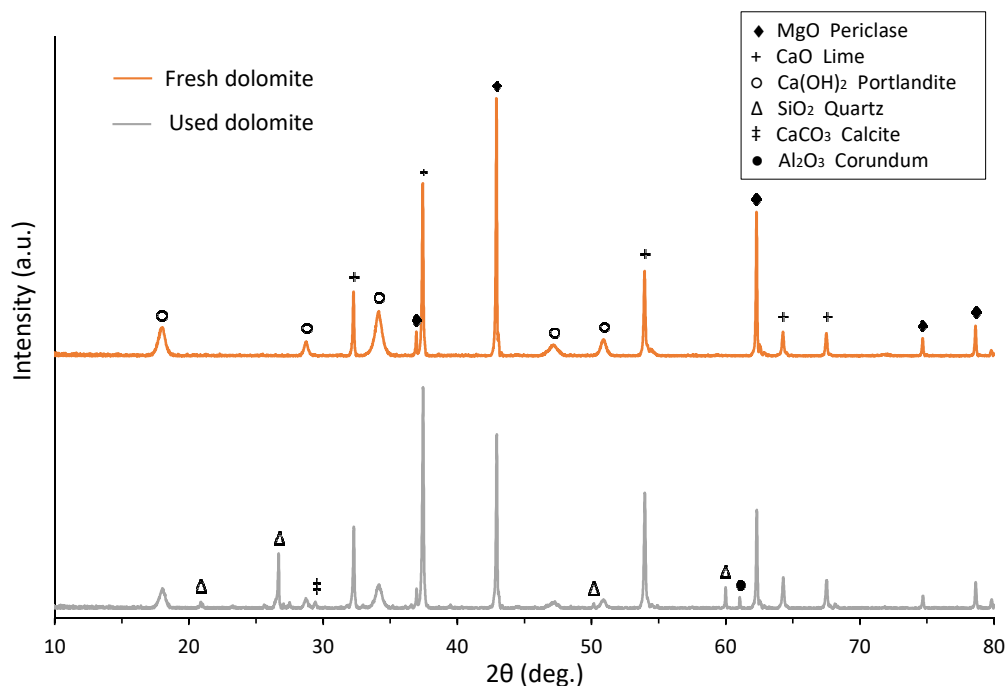
<b>Element (wt.%)</b>	<b>Fresh dolomite</b>	<b>Used dolomite</b>
Loss on ignition (wt.%)	9.01	11.88
SiO <sub>2</sub>	0.53	4.35
Al <sub>2</sub> O <sub>3</sub>	0.26	1.02
Fe <sub>2</sub> O <sub>3</sub>	0.39	0.43
MnO	0.02	0.14
MgO	38.30	34.16
CaO	50.13	47.20
Na <sub>2</sub> O	0.02	0.04
K <sub>2</sub> O	0.01	0.28
TiO <sub>2</sub>	0.02	0.05
P <sub>2</sub> O <sub>5</sub>	0.03	0.39

238

### 239 *3.1.2. XRD characterization of the catalysts*

240

241 As observed in [Figure 2](#), the diffraction peaks of fresh dolomite show the presence of  
 242 periclase (MgO), lime (CaO), and portlandite (Ca(OH)<sub>2</sub>). The peaks representative of dolomite  
 243 structure (CaMg(CO<sub>3</sub>)<sub>2</sub>) are not detected. This crystalline modification can be explained by the  
 244 effect of the calcination treatment initially applied to this material, which is in agreement with  
 245 previous studies [45,65]. The XRD spectrum of used dolomite reveals the formation of  
 246 significant amounts of quartz (SiO<sub>2</sub>) and traces of corundum (Al<sub>2</sub>O<sub>3</sub>). This evolution corroborates  
 247 the ICP and SEM-EDX results demonstrating the enrichment of ash-based species in dolomite  
 248 particles during biomass gasification. XRD analysis also shows a relative decrease of MgO vs.  
 249 CaO in used dolomite. A small peak of calcite is detected in the used dolomite probably due to a  
 250 limited carbonation at 750°C in the gasifier (around 15%vol. of CO<sub>2</sub> at the exit of the fluidised  
 251 bed).



252

253

Figure 2. Diffractogram of the fresh and used dolomites

254 *3.1.3. Composition of the surface by XPS*

255

256 The XPS results are presented in Table 4. Binding energy (BE) and atomic concentration  
 257 (%) were ascribed to the element according to published data [45,94,95].

258 For fresh dolomite, the binding energies of the C 1s signal (Table 4) highlight the  
 259 presence of various carbonaceous species: graphitic or/and aliphatic hydrocarbons (C-C, C-H) at  
 260 284.6 eV, ethers (C-O) at 286.02 eV, aldehydes or carboxylic acids (C=O) at 287.89 eV, and  
 261 carbonates ((CO<sub>3</sub>)<sup>2-</sup>) at 289.40 eV. Carbonates are part of the dolomite composition and are  
 262 present in higher relative amount on the surface than in the bulk (as shown by XRD) mainly  
 263 explained by the exposure to air (at room temperature) of the decarbonated samples. The other  
 264 carbon species than carbonates may be attributed to carbonaceous deposit [94].

265

266 Two oxygen species were observed through the O 1s binding energies at 531.17eV and  
 267 532.80 eV. The first one corresponds to O-C or O-H bonds, related to the presence of both  
 268 carbonaceous and hydroxyl species [95]. These 2 types of bonds unfortunately cannot be  
 269 discriminated. The second O 1s signal at 532.80eV is generally attributed to chemisorbed water  
 270 [95]. However, the high percentage of 40.47% is much higher than that of the carbonaceous  
 271 species identified by the C-O bonding at 286.02 eV. Therefore the O 1s binding at 531.17eV may  
 272 rather correspond to structural hydroxyls of the fresh catalyst. Its surface would be highly  
 273 hydroxylated probably due to room temperature storage.

274 The Mg 2*p* and Ca 2*p* signals correspond to surface concentrations (13.56 and 1.86%  
 275 respectively) much lower than the bulk oxides as analyzed by ICP. This result may be related to  
 276 the highly hydroxylated surface of the catalyst.

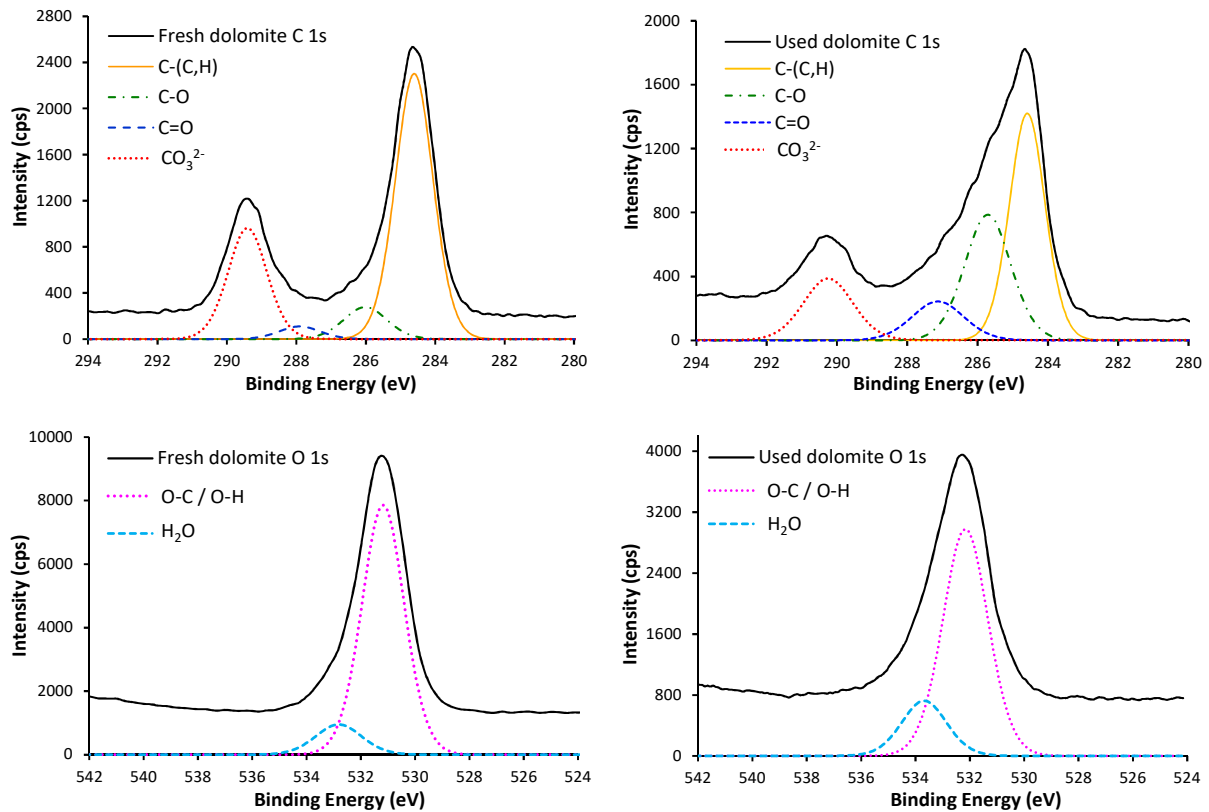
277 While iron and aluminium were observed in the bulk by ICP (0.4 and 1.0%, respectively),  
 278 these elements are not detected at the surface of dolomite by XPS (before and after gasification).  
 279 Their content may be beyond the detection limit of the XPS technique, or these species could be  
 280 mainly located in the bulk and not at the external surface analysed by XPS.

281 Concerning the used dolomite, silica species are found at the surface (1.0%) which is  
 282 consistent with SEM-EDX analysis. The Mg 2*p* and Ca 2*p* intensity peaks decrease after  
 283 gasification: their atomic ratio dropped from 13.56 to 9.72 at.% for Ca, and from 1.86 to 1.00  
 284 at.% for Mg (Table 4). This relative decrease in Ca and Mg is consistent with the bulk analysis by  
 285 ICP measurements (Table 3).

286 **Table 4. XPS analysis of fresh and used dolomites**

Element	Fresh Dolomite		Used Dolomite	
	BE (eV)	at.%	BE (eV)	at.%
O 1s O-C/O-H	531.17	40.47	532.16	27.59
O 1s H <sub>2</sub> O	532.80	5.33	533.66	6.68
C 1s C-(C,H)	284.60	23.88	284.59	23.00
C 1s C-OR, C- OH, C-O	286.02	3.32	285.72	16.49
C 1s C=O	287.89	1.25	287.14	5.75
C 1s CO <sub>3</sub> <sup>-2</sup>	289.40	10.33	290.24	8.74
Ca 2 <i>p</i>	346.80	13.56	347.75	9.72
Mg 2 <i>p</i>	49.40	1.86	50.35	1.03
Si 2 <i>p</i>	-	-	101.25	1.00

287 The evolution of the oxygenated and carbonaceous species observed with XPS after gasification  
 288 is illustrated in Figure 3. After gasification the atomic concentration of carbon at the surface of  
 289 used dolomite significantly increases (from 38.8 to 53.9 wt.%), and the concentration of oxygen  
 290 drops from 45.8 to 34.3 wt.%. Carbonaceous species containing ethers or carboxylic functions  
 291 strongly increase after gasification (from 3.32 to 16.49%, and from 1.25 to 5.75%, respectively)  
 292 probably due to oxygenated carbon deposit (Table 4). The content of hydrocarbons originally  
 293 contained in the dolomite structure (C 1s C-(C-H)) is almost unchanged. The concentration of  
 294 carbonates (C 1s CO<sub>3</sub><sup>2-</sup>) decreases a little after gasification. O 1s signal considerably decreases  
 295 after gasification. Globally, after gasification, the surface becomes richer in C-O species and  
 296 poorer in Ca-O and Mg-O.



298

299 **Figure 3.** XPS spectra of carbon (C 1s) and oxygen (O 1s) species analysed on fresh dolomite and  
 300 used dolomite after gasification.

301 TPD and TPO experiments were performed in order to complete these XPS analysis and to get a  
 302 better insight on the nature of carbonaceous species present in fresh and used dolomites.

### 303 3.1.4. TPD and TPO characterizations

304

305 The amounts of CO<sub>2</sub> released by fresh and used dolomite during TPD and TPO analysis  
 306 are presented in [Figure 4 \(A\) and \(B\)](#) respectively.

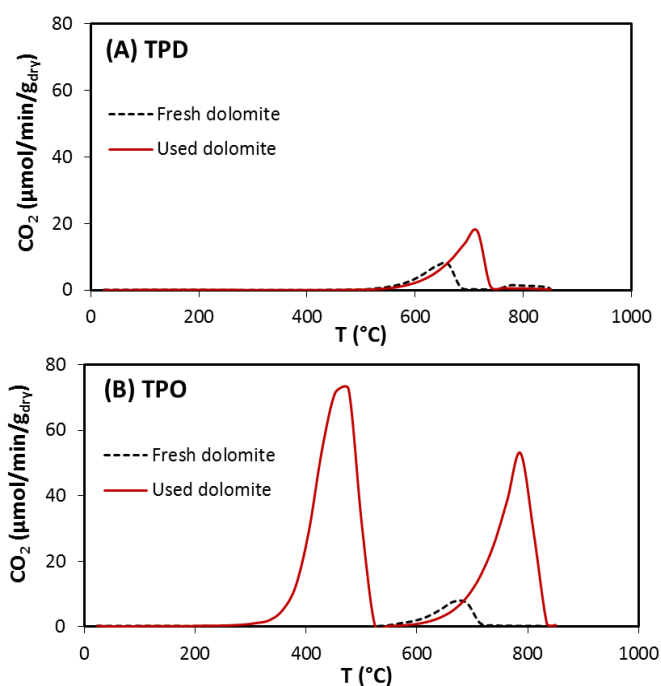
307

308 No carbon monoxide was released during these analyses. During TPD ([Figure 4A](#)), both  
 309 samples display a single CO<sub>2</sub> peak occurring at a similar temperature (between 500 and 750°C).  
 310 The maximum peak is at 660°C and 715°C for fresh dolomite and used dolomite, respectively.  
 311 The CO<sub>2</sub> release obtained under pure nitrogen atmosphere is attributed to the decomposition of  
 312 carbonates present in both samples. It can be noted that the amount of CO<sub>2</sub> desorbed was  
 313 significantly higher for the used dolomite, which could be explained by the formation of  
 314 carbonates during the gasification reactions. This is in agreement with XRD analysis ([Figure 2](#)).

314

315 During the TPO analysis, a significant CO<sub>2</sub> peak is obtained at low temperature (460°C)  
 for used dolomite ([Figure 4B](#)). This peak results from the oxidation of a reactive carbon

316 produced during gasification. In addition, a CO<sub>2</sub> peak similar to that obtained during the TPD  
317 tests is observed for both samples. However, for used dolomite, the maximum of this peak is  
318 achieved at slightly higher temperature than during TPD (790°C vs 715°C), and the amount of  
319 CO<sub>2</sub> released is much higher. This difference can be attributed to the oxidation of a more stable  
320 coke produced during the gasification reactions and oxidized at high temperature (≈800°C). To  
321 the best of our knowledge we present here the first TPO analysis of a dolomite used in a pilot  
322 scale gasifier during a significant time (10 days).  
323



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Figure 4. (A) TPD and (B) TPO analysis of fresh and used dolomites.

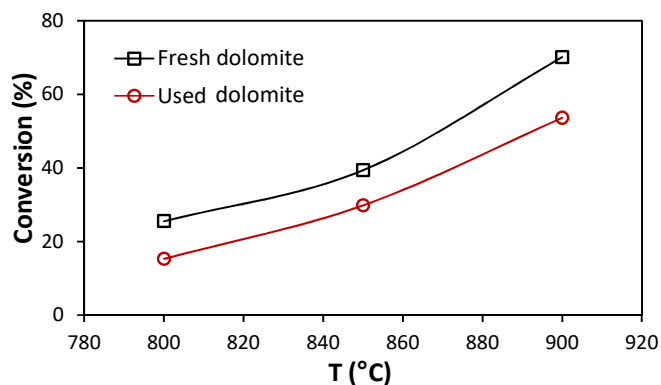
328

329 It is interesting to notice that similar ratios of carbonates to total carbon [ $C_{\text{Carbonates}}/C_{\text{total}}$ ]  
330 were found between TPD/TPO ( $C_{\text{Carbonates}}/C_{\text{total}}=0.13$ ) and XPS ( $C_{\text{Carbonates}}/C_{\text{total}}=0.16$ ) for the  
331 used dolomite. This would mean that the evolution of CO<sub>2</sub> analysed during TPD/TPO may  
332 account for the decomposition of functions (carbonates and coke deposit) which are mainly  
333 formed at the external surface of particles during biomass gasification.

### 334 3.2. Steam reforming of benzene over fresh and used dolomites

335 In order to “probe” the reactivity of the two dolomite samples, their catalytic activity for  
336 benzene steam reforming were compared at three temperatures (800, 850 and 900°C). The  
337 evolution of benzene conversion is presented in Figure 5.

338 For both dolomites, the increase in temperature increases the benzene conversion.  
339 Indeed, the conversion of benzene is multiplied by 3.5 between 800 and 900°C. It is interesting  
340 to note that used dolomite is less active than the fresh one. The activity of used dolomite  
341 decreases by about 25% compared to the fresh sample. At 900°C the conversion of benzene  
342 obtained with fresh dolomite reaches 70% against 54% with used dolomite.  
343



344  
345 **Figure 5. Effect of temperature and dolomite aging on benzene conversion during steam**  
346 **reforming ( $C_6H_6=0.5$  vol%,  $H_2O=22.2$  vol% in  $N_2$ , 3 g dolomite, 45 NmL/min total flow rate).**

347 To assess the effect of aging on the reaction mechanisms, the selectivity on reaction  
348 products has been determined (Table 5). Similar gaseous species were produced by fresh and  
349 used dolomites:  $H_2$ ,  $CO_2$ ,  $CO$ , and  $CH_4$ . For both samples, the main products were  $H_2$  and  $CO_2$ .  
350 Traces of  $C_2H_4$  were produced by steam reforming of benzene only over the fresh dolomite.

351 For fresh dolomite, rising temperature from 800 to 900°C results in a decrease of  $H_2$  (-  
352 3.9%) and  $CO_2$  (-2.3%) selectivities at the expense of  $CO$  (+3.7%) and  $CH_4$  (+2.5%). This means  
353 that the overall selectivity in products is not mainly controlled by the thermodynamic equilibrium  
354 of the water gas-shift reaction which promotes  $H_2$  and  $CO_2$  at lower temperatures. The increase  
355 in  $CO/CO_2$  with temperature is in agreement with results reported by *Constantinou et al.* in a  
356 stream rich in  $H_2$  [45]. At higher temperature, the cracking reaction of benzene forming  $CH_4$   
357 seems to be promoted. The decrease in  $H_2$  selectivity with temperature may be linked to the  
358 higher selectivity in  $CH_4$ . Further discussion is provided after the presentation of a potential  
359 mechanism of benzene reforming over dolomites in the next section.

360

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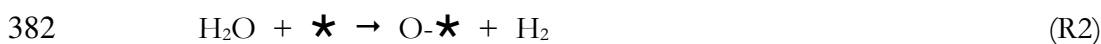
Table 5. Molar selectivity of the products generated by steam reforming of benzene.

	H <sub>2</sub> (mol%)			CO <sub>2</sub> (mol%)			CO (mol%)			CH <sub>4</sub> (mol%)			C <sub>2</sub> H <sub>4</sub> (mol%)		
	800	850	900	800	850	900	800	850	900	800	850	900	800	850	900
T (°C)	800	850	900	800	850	900	800	850	900	800	850	900	800	850	900
Fresh dolomite	66.9	65.8	63.0	25.7	25.2	23.4	1.9	3.1	5.6	3.0	4.4	5.5	0.8	0.9	0.6
Used dolomite	65.5	66.9	66.5	30.7	27.4	22.4	2.6	3.5	8.3	1.2	2.2	2.9	0.0	0.0	0.0

364 Concerning the used dolomite, the evolutions of CO<sub>2</sub> and CO are more significant with  
365 rising temperature: -8.3% and +5.6%, respectively. Contrary to the fresh dolomite, the selectivity  
366 in H<sub>2</sub> was almost constant with rising temperature. This finding confirms that the equilibrium of  
367 water gas-shift reaction does not control the global selectivity in CO<sub>2</sub>/H<sub>2</sub>/CO in this case. The  
368 steam gasification of coke present in the used dolomite (deposited during biomass gasification  
369 and as analyzed by TPO) may also contribute the higher selectivity in H<sub>2</sub> and CO notably at  
370 900°C. More complex phenomena occur and will be detailed in the next section. The selectivities  
371 in CH<sub>4</sub> and in C<sub>2</sub>H<sub>4</sub> are lower for the used dolomites. This result may be explained by a lower  
372 cracking rate of benzene over the used dolomite.

### 373 3.3. Discussion on the reaction mechanisms

374 In a deep study *Alarcon et al.* have proposed a detailed mechanism for the steam reforming of  
375 aromatics over CaO and MgO [68]. These authors have proposed, by analogy with the  
376 mechanism of hydrocarbons steam-reforming over metal supported catalysts [96], that aromatic  
377 hydrocarbons reforming over CaO or MgO catalysts would take place in two main step [94]: (i)  
378 the decomposition of the hydrocarbon and the water on the catalyst surface, and then (ii) the  
379 gasification of the deposited carbon with steam. The overall process could be written according  
380 to the following simplified mechanism:



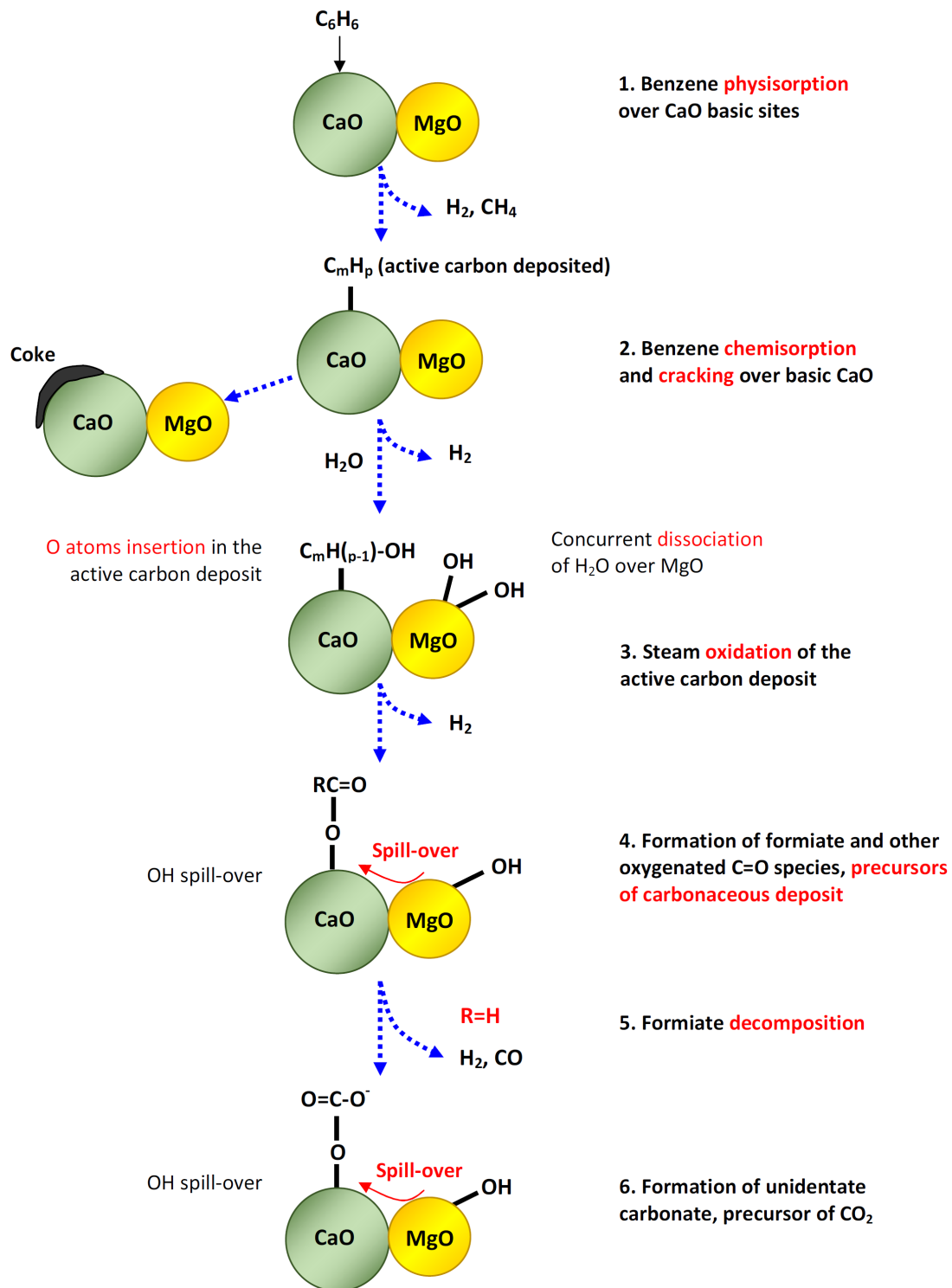
384 where ArH is an aromatic hydrocarbon specie,  $\star$  is a M<sup>2+</sup>O<sup>2-</sup> unit (the active site in  
385 dolomite). The deposit (C<sub>x</sub>H<sub>y</sub>-) may also decompose into smaller fragments and further form H<sub>2</sub>,  
386 CH<sub>4</sub>, and C<sub>x</sub> [68,94].

387 The decomposition of water molecules to hydrogen is easy over metal supported catalyst  
388 when the metal phase is a noble or transition metal [96]. This is much less likely to occur over the



389 non-reducible CaO or MgO oxides, unless they contained catalytic traces of a transition metal (e;  
390 g; iron). Contrary to the reaction (R2) proposed by a previous study, we rather think that gaseous  
391 H<sub>2</sub> stems from the decomposition of gaseous water on the carbon fragments rather than from  
392 the direct water decomposition on the metal oxides. In other words, the water molecules are  
393 reduced by the surface carbon fragments but not by the fixed valence metal oxides.

394           Based on our results and on literature analysis [45,68,74,94,97], an overall mechanism of  
395 benzene steam reforming over dolomite is proposed ([Figure 6](#)).



396  
 397 Figure 6. Chemical mechanism of benzene steam reforming over dolomite proposed based on  
 398 the experimental results of the present study and on previous works [45,68,74,94,97].  
 399

400 First, a theoretical investigation of benzene adsorption over calcite and dolomite dry  
 401 surfaces reported that Ca sites are the most energetically favorable for hydrocarbon adsorption

402 on both minerals [98]. Moreover, van der Waals interactions increase the stability for all sites but  
403 more strongly on the Ca site. The benzene molecule was found to be adsorbed in a Ca hole, the  
404 aromatic ring forming an angle of 15 to 35° with the surface. For MgO, benzene adsorption takes  
405 place on weakly acidic OH groups, rather than on the Mg sites. The rate determining step of the  
406 steam-reforming of benzene over dolomite is the adsorption of the reactant hydrocarbon  
407 molecule [69]. This can be explained by the interactions between a neutral molecule and a  
408 strongly polarized solid surface. The stable and symmetrical benzene molecule is not easily  
409 polarizable, even with the highly ionic CaO or MgO dipoles. As a result, the chemical adsorption  
410 is weak and the Van der Waals interactions may become important [99]. From hard and soft acids  
411 and bases principles [100,101], benzene is a soft base and  $\text{Ca}^{2+}$  a hard acid, also their interaction is  
412 fundamentally expected to be very poor. This interaction should be of van der Waals type, in  
413 good accordance with the theoretical investigation reported by *Rigo et al.* [98]. From these studies,  
414 it can be proposed that benzene is rather adsorbed and decomposed on the calcium oxide by  
415 interaction with the  $\text{Ca}^{++}$  component (Figure 6).

416 Second, concerning the adsorption and role of water, MgO, CaO and other non-reducible  
417 oxides (activated at high temperatures) exhibit the presence of highly basic  $\text{O}^{2-}$  sites [97]. The OH  
418 groups were shown to exist in the naphthalene steam-reforming reaction conditions over pure  
419 MgO or MgO+CaO mixture, but not over pure CaO [68]. On the other hand, the introduction  
420 of steam results in the disappearance of the carbonaceous matter (mainly in the form of formiate  
421 species) from the surface of pure MgO and MgO-containing mixture, while formiate species  
422 remains in the surface of CaO catalyst [68]. The authors concluded that the OH groups,  
423 stemming from MgO, could participate both to the gaseous products formation and to coke  
424 removal. Chemically, it is impossible that anionic OH groups directly participate to the oxidation  
425 of carbons belonging to C-C or C-H  $\sigma$  bonds. Thus,  $\text{OH}^-$  cannot be active species in the benzene  
426 steam-reforming. On the contrary,  $\text{H}_2\text{O}$  may be responsible for the direct oxidation of  
427 hydrocarbons ( $\text{C}_m\text{H}_{(p-1)}\text{-OH}$ ) (Figure 6). Due to its chemical properties,  $\text{OH}^-$  can be reactive  
428 towards the oxidation of the carbon of C=O double  $\pi$  bonds of oxygenate species by a  
429 nucleophilic attack. The presence of these species over alkaline oxides were evidenced by *Alarcon*  
430 *et al.* [94]. These species disappear from the surface after the introduction of steam in the reactor  
431 over MgO or CaO+MgO, but not over pure CaO. This led us to conclude that the role of MgO  
432 in MgO+CaO mixture (and therefore in dolomite) is to bring the OH groups for the oxidation of  
433 oxygenate species deposited over CaO (after benzene sorption). This reaction would occur at the  
434 MgO-CaO interface or through the spillover effect of the OH groups [102] (Figure 6).

435 In an investigation on MgO [99] prepared from Mg(OH)<sub>2</sub> precursor treated at various  
436 temperatures, it was shown that the surface OH concentration was similar for small or large MgO  
437 particles, but that the latter allowed more germinal OH pairs as well as OH surface island  
438 domains with weak Brönsted acidity. The reactivity of the OH groups is thus related to the  
439 morphology of MgO which, in turn, depends on the nature of the precursor and pre-treatments.  
440 This may contribute to the difference of reactivity of MgO in MgO+CaO mechanical mixture,  
441 and dolomite.

442 Therefore in our proposed mechanism (Figure 6), the first step consists in the adsorption  
443 of benzene over the basic site of CaO [98] to form an active carbon deposit (C<sub>m</sub>H<sub>p</sub>), C<sub>x</sub>H<sub>y</sub> gas  
444 species (as analyzed in our work), and H<sub>2</sub>. Then, the active carbon deposit can produce coke.  
445 Water may either directly oxidize this active carbon deposit or may be dissociatively chemisorbed  
446 over MgO active site to form OH basic species. These OH basic species contribute to the  
447 formation of formiate and other oxygenate intermediates, then forming unidentate carbonate  
448 through OH spill-over. Formiate and carbonates have been analyzed by XPS in this present work  
449 and by infrared spectroscopy by *Alarvon et al.* [68,94] and *Constantinou et al.* [45]. This mechanism  
450 corroborates the results of *Constantinou et al.* [45] who demonstrated that OH species are  
451 important reaction intermediates for the conversion of aromatics into C<sub>x</sub> and H<sub>2</sub>. It has also been  
452 proved that unidentate carbonates are less stable than bicarbonates and constitute the main  
453 species formed over dolomite [45,68,103]. The former would be the precursors in CO<sub>2</sub>  
454 formation.

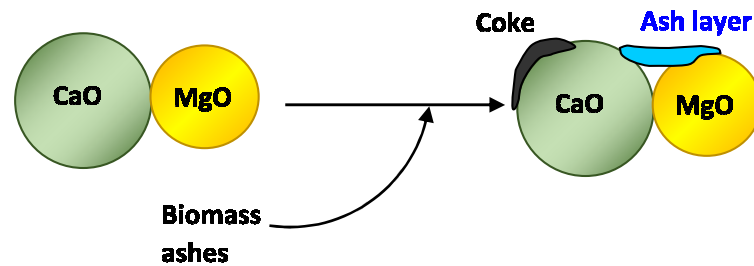
455 The proposed mechanism supports our experimental results. When the temperature  
456 increases, the cracking of benzene promotes the formation of C<sub>x</sub>H<sub>y</sub> gas species, especially over  
457 fresh dolomite. This reaction is less favored with the used dolomite probably due to the lower  
458 availability of CaO sites (as analyzed by XPS). The temperature increase is also associated to a  
459 decrease in CO<sub>2</sub> and an increase in CO selectivities (Table 5). This evolution maybe explained by  
460 the cracking of benzene, as well as by the complex coupling between OH species formation and  
461 spill-over leading to CO/CO<sub>2</sub> (from formiate and carbonate intermediate). Carbon monoxide is  
462 generated by the thermal decomposition of formiate and higher homologs. This reaction was  
463 enhanced by increasing temperature, at the expense of the carbonates and CO<sub>2</sub> route. Indeed, at  
464 high temperature, this route (formation of OH by H<sub>2</sub>O dissociation on MgO sites, and OH spill-  
465 over) maybe slower than the formiate thermal decomposition microkinetic rate. Therefore the  
466 OH source may be limited leading to a lower formation of CO<sub>2</sub> from carbonate. This effect is  
467 even more marked for the used dolomite since MgO sites, required for OH species formation,  
468 are expected to be less available. The CO<sub>2</sub> route is also inhibited by increasing cracking reactions

469 with rising temperature. Further studies are needed to study more deeply the detailed chemistry  
470 of these intermediate C-O species at the temperatures of hydrocarbons steam reforming.

471

472 For used dolomite, the deposit of coke and ashes, detected in this study by various  
473 analytical tools, reduced the global availability of CaO and MgO active sites, as presented in the  
474 simplified scheme in Figure 7.

475



476

477 Figure 7. Deactivation of dolomites in biomass gasification reactors: the ashes formed from  
478 biomass oxidation leads to a deposit of Si (and other species present in ashes) layer over  
479 dolomite, and coke deposit also reduces the available active sites for benzene and water  
480 adsorption.

481

482

483

#### 484 **4. Conclusion**

485           The evolution of dolomite surface chemistry during its use as bed material in a pilot-scale  
486 gasification reactor and its resulting activity on tar reforming have been studied for the first time.  
487 Benzene steam reforming was selected as a model reaction in order to probe the activity of the  
488 dolomites.

489           BET, SEM-EDX, XRD, XPS, and TPO/TPD analyses revealed a drastic change of the  
490 surface properties of used dolomites. After being used as a bed material, used dolomite was  
491 covered by a layer rich in Si from biomass ash. In addition, coke was deposited at the used  
492 dolomite surface after gasification reactions.

493           The catalytic activity of used dolomite was  $\approx 24\%$  lower than that of fresh dolomite. This  
494 drop in catalytic activity can be attributed to the Si-rich layer covering the surface of used  
495 dolomite together with the coke deposition which decreased the availability of the active sites  
496 (CaO, MgO). In addition, SiO<sub>2</sub> has low catalytic activity towards tar reforming reactions. The  
497 SiO<sub>2</sub> and coke deposition could also limit the interactions between CaO and MgO, thus allowing  
498 the production of stable coke deactivating the catalyst.

499           This study presents a methodological approach that can be further used to study the  
500 effect of different operating conditions during biomass gasification on the activity and  
501 composition of dolomites (or other materials). Based on our experimental results and on the  
502 literature data, a new reaction mechanism of benzene steam reforming on fresh and used  
503 dolomite was proposed.

504

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509

510

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Graphical abstract

