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1     **Hydrodeoxygenation of guaiacol into cyclohexane over mesoporous silica**  
2                                     **supported Ni-ZrO<sub>2</sub> catalyst**

3  
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16 **Abstract**

17 Ordered mesoporous silica SBA-15 and KIT-6 supported Ni/ZrO<sub>2</sub> catalysts are evaluated  
18 for the hydrodeoxygenation of guaiacol (stirred batch reactor, 300 °C, 50 bar of H<sub>2</sub>),  
19 guaiacol being a model compound of bio-oil issued from the lignin fraction of biomass  
20 liquefaction step. ZrO<sub>2</sub> and Ni are dispersed using incipient-wetness impregnation (IWI) or  
21 two-solvent (TS) method over mesoporous silica. Mesoporous zirconia (nanocasting  
22 method) and conventional zirconia were also used as supports. Cyclohexane, cyclohexanol  
23 and methoxycyclohexanol are the main products of reaction. Significant differences in  
24 cyclohexane yield are measured (after 8 h reaction, with conversion in most cases above  
25 85%): NiZr-KIT-TS, 71.6% > NiZr-SBA-TS, 63.3% >> Ni/meso-Zr, 7.8% > NiZr-SBA-  
26 IWI, 5.2% > Ni/ZrO<sub>2</sub>, 1.6%. Tetragonal ZrO<sub>2</sub> phase, acting as oxophilic phase for guaiacol  
27 / oxygenated intermediates adsorption and activation, is observed whatever the approach  
28 selected for the preparation. However, when nickel is supported over pure zirconia, low  
29 selectivity to cyclohexane is obtained, while the main product becomes cyclohexanol with  
30 yields reaching ~40%. Better activities and selectivities toward total deoxygenation  
31 (cyclohexane production) are obtained for the silica supported Ni-ZrO<sub>2</sub> catalysts, especially  
32 when the catalyst is prepared by the two-solvent approach. Improvement is associated to  
33 the proximity between Ni and ZrO<sub>2</sub> particles when confined in the silica mesopores.  
34 Finally, conversion and yield to cyclohexane obtained with NiZr-KIT-TS are stable during  
35 5 successive catalytic cycles demonstrating the absence of significant modification of the  
36 catalyst during reaction. These results are evidencing that the confining strategy is efficient  
37 to improve stability of active elements during HDO reaction.

38

39

40 **Keywords:** ZrO<sub>2</sub>; Ni; mesoporous silica; hydrodeoxygenation; guaiacol; biomass.

41

## 42 **1. Introduction**

43 Lignocellulosic biomass is a renewable and abundant feedstock, considered as an important  
44 raw resource for the biorefineries. Thermal and thermochemical processes are sustainable  
45 methods for producing bio-oils, from which chemicals and fuels can be obtained [1, 2].  
46 Bio-oils are composed of a significant fraction of oxygenated aromatic compounds (up to  
47 40%) [3], having a high potential for the production of chemical derivatives [4].  
48 Unfortunately, the aromatic nature and the high oxygen content of the raw bio-oil results in  
49 inadequate properties for a direct fuel valorisation (high viscosity, high acidity, low  
50 stability, low heating value [5-7]). Oxygen content decrease is a key step in the upgrading  
51 of the lignocellulosic derived bio-oil, in order to obtain valuable products such as alkanes  
52 and aromatics. Among the different available processes, the catalytic hydrodeoxygenation  
53 (HDO) has gained considerable attention during the past two decades. HDO reaction is  
54 generally conducted at temperatures between 150 and 500 °C, and under H<sub>2</sub> pressure (up to  
55 3 MPa), in the presence of a heterogeneous catalyst [8-10]. Considering the severe reaction  
56 conditions, and the production of water and CO/CO<sub>2</sub> (reaction products), robust catalysts  
57 are needed [11].

58 HDO studies are often conducted over model compounds such as guaiacol, anisole and  
59 other phenolic compounds [12, 13]. Guaiacol, 2-methoxyphenol, is an oxygenated  
60 compound representative of the phenolic fraction contained in bio-oils derived from lignin  
61 [12, 14, 15]. Besides, the cleavage of the aromatic methoxy group and of the hydroxy group  
62 of guaiacol (both major functional groups of lignin-derived phenolic compounds) is  
63 complex since the reactivity of products under the applied reaction conditions can lead to  
64 polymerization reactions, and consequently organic matter accumulation on the catalyst  
65 surface [16] that causes catalyst deactivation. Consequently, high selectivity in  
66 deoxygenated compounds can be obtained only under careful control of operational  
67 parameters and catalyst properties [16, 17]. Among the catalyst functions needed, metal  
68 phase acts for hydrogen activation but metal only is not sufficient to obtain satisfying  
69 selectivities to deoxygenated compounds. Acid / oxophilic sites are also needed to improve  
70 deoxygenated products selectivities, and can also lead to an activity increase [18-20].  
71 Sulfided MoS<sub>2</sub>, CoMo-S, NiMo-S (hydrotreating catalysts) [21-25] and unsupported /

72 supported ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , activated carbon,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or zeolites) metal nitrides such as  
73  $\text{Mo}_2\text{N}$  [26, 27] were then proposed for the reaction. Over sulphide catalysts, the presence of  
74 oxygen and water led to rapid catalyst deactivation [21, 22, 24]. Sulfur-containing  
75 molecules (dimethyldisulfide (DMDS),  $\text{H}_2\text{S}$ ) has to be added in the reaction feed to obtain  
76 better stability [21, 28, 29]. Supported noble metals - Pt, Pd, Ir, Ru or Rh - are also  
77 effective catalysts [30-32], as well as Ni [31-34]. Using acidic catalysts (containing both  
78 Brønsted or Lewis sites) allows to modulate reaction selectivity with these metals [30, 35-  
79 37], inhibiting hydrogenation of oxygenated intermediates [35] or achieving complete  
80 deoxygenation [30, 36]. Aromatic ring, bearing oxygenated functional groups, is adsorbed  
81 and activated on the oxophilic / acidic surfaces, in orientations favoring the C-O bond  
82 activation and breaking [18, 21, 37-39]. According to different theoretical models, supports  
83 like  $\text{SiO}_2$  favors adsorption of phenol ring on three different modes i)  $\pi$ -interaction, ii) flat  
84 O-interaction and iii) perpendicular O-interaction, although the adsorption mode depends  
85 on the surface structure of the silica [40]. For instance, on  $\text{Fe}/\text{SiO}_2$  catalyst,  $\text{H}_2$  molecule is  
86 dissociatively adsorbed on metallic Fe sites while guaiacol [41] or phenol [40] is adsorbed  
87 on closest silanol groups of weak acidity to be hydrogenated. For several catalyst  
88 formulations, stability remains a drawback. Using monometallic or bimetallic noble metal-  
89 based catalysts, rapid catalyst deactivation generally occurs [21, 42-44]. Carbon  
90 accumulation is, in part, at the origin of the activity decrease [45], and active phase  
91 sintering [46], accumulation of oxygen containing molecules on catalyst surface [46] are  
92 other identified reasons. In addition to Ni, non-noble metals such as Cu [47], Mo [48, 49]  
93 and Fe [41, 50], in addition to transition metal phosphides [51, 52] and carbides [53] were  
94 also proposed as alternative catalysts. While the metals always promote the hydrogenation  
95 reactions, Lewis or Brønsted [37, 54]; presence of oxophilic surface sites ( $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$ ) [55,  
96 56], the metal itself (case of Ni [57]); the oxygen surface vacancies density affording C-O  
97 bond activation [58-60].

98 Among the possible supports, transition alumina is not enough stable toward water [61].  
99  $\text{ZrO}_2$  or  $\text{TiO}_2$  appear more appropriate due to oxophilic surface properties, but commercial  
100 supports exhibit low surface areas which is detrimental to the dispersion of active metals  
101 [62]. An open stable porosity is preferable [63], a characteristic which fits with ordered  
102 mesostructured materials. Among, some of them exhibit satisfying hydrothermal stability

103 [64-66]. Additionally, the presence of large mesopores is also favorable to reactant  
104 diffusion to active sites, leading to efficient mass transfer [67, 68]. As aforementioned,  
105 silica is an adequate support for HDO reaction, considering that the amorphous silica  
106 surface of low silanol concentration will ensure a catalyst suffering from limited inhibition  
107 by water and CO, while phenolic compounds will adsorb on surface silanol in favorable  
108 configuration [40, 69]. HDO of vanillin was then reported using 5 wt.% Pd/KIT-6 [68]. A  
109 98% vanillin conversion with 94% selectivity toward p-cresol (300 °C, 6 h, flow = 50 mL  
110 min<sup>-1</sup>, WHSV of 21.2 h<sup>-1</sup>) is reported. HDO of anisole was also studied over Ni/SBA-15 or  
111 Co/SBA-15, Ni-based catalyst exhibiting high selectivity toward methoxycyclohexane  
112 (~80%) at complete anisole conversion (300 °C, 10 bar of H<sub>2</sub>) [70]. Al-modified silica also  
113 presents adequate surface properties. Over Pt/Al-SBA-15 (Si/Al = 20), 70% guaiacol  
114 conversion with a 43% cyclohexane yield (250 °C for 2 h, 400 rpm, 40 bar of H<sub>2</sub>) was  
115 reported by Yu et al. [71]. Rh-Ni over Al-KIT-6 silica is also an efficient catalyst for the  
116 HDO of diphenyl ether and guaiacol [72]. Literature dealing with non-siliceous mesoporous  
117 materials as supports in HDO reaction is rather more limited [73].

118 In this work, ordered mesoporous silica SBA-15 and KIT-6 were used as supports to  
119 disperse Ni-ZrO<sub>2</sub> particles, and to prepare mesoporous ZrO<sub>2</sub> supported Ni catalyst.  
120 Catalysts were tested for the HDO of guaiacol reaction, a model oxygenated molecule of  
121 lignin-derived bio-oil. The results show that the approach selected for the deposition of Ni  
122 and ZrO<sub>2</sub> phases is of paramount importance. High selectivity toward cyclohexane (~80%)  
123 at high guaiacol conversion (>90%) can then be obtained over silica composites prepared  
124 by the two-solvent impregnation approach.

## 125 **2. Experimental**

### 126 **2.1. Mesoporous SBA-15 and KIT-6 silica support synthesis**

127 SBA-15 silica was synthesized using classical hydrothermal procedure, using the nonionic  
128 triblock copolymer surfactant P123 (PEO20-PPO70-PEO20, MW = 5800 g mol<sup>-1</sup>, BASF)  
129 [74, 75]. 12.0 g of P123 were dissolved in a solution containing 360 g of ultrapure water  
130 and 37.2 g of concentrated hydrochloric acid (37 wt.%). The solution was heated at 35 °C.  
131 24.0 g of tetraethyl orthosilicate (TEOS, Merck, 98%) were added, and the mixture was

132 aged at 35 °C during 24 h. Then, the suspension was hydrothermally treated at 140 °C  
133 during 24 h. The solid was recovered by filtration without washing, air-drying at 80 °C, and  
134 final calcination at 550 °C for 3 h under static air (heating rate = 1 °C min<sup>-1</sup>).

135 KIT-6 silica was synthesized, using the same soft template, P123 [76]. 6.0 g of P123  
136 surfactant were dissolved in a solution containing 217 g of ultrapure water and 11.7 g of  
137 concentrated hydrochloric acid (37 wt.%) at 35 °C. Thereafter, 6.0 g of 1-butanol (Merck,  
138 99%) were added and the resulting solution was stirred for 1 h before the addition of 12.9 g  
139 of TEOS. The resulting solution was aged at 35 °C during 24 h, and hydrothermally treated  
140 at 100 °C during 24 h. Recovery and activation procedures were exactly the same than  
141 applied for the SBA-15 support.

## 142 **2.2. Preparation of silica supported Ni-ZrO<sub>2</sub> catalysts**

143 Impregnation of ZrO<sub>2</sub> and NiO in the silica supports was performed using two different  
144 impregnation procedures: (i) Incipient-Wetness Impregnation, IWI, leading to NiZr-SBA-  
145 IWI catalyst; (ii) Two-Solvents impregnation [77], TS, leading to NiZr-SBA-TS and NiZr-  
146 KIT-TS. The nominal Zr and Ni loadings were 15 and 10 wt.%, respectively.

147 *Case of IWI procedure:* aqueous solutions were prepared for nickel (S1) and zirconium (S2)  
148 precursors. Solution S1 was prepared by dissolving Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma–Aldrich,  
149 ≥98.5%, p.a. grade) and solution S2 by dissolving ZrO(CO<sub>3</sub>)·xH<sub>2</sub>O (Amuco Inc. ≥40%  
150 ZrO<sub>2</sub>) in water. Solution S2 was slowly dropped onto 2.0 g of freshly calcined SBA-15  
151 support. After homogenization, the solid was dried at 80 °C during 12 h and finally  
152 calcined under static air at 700 °C (temperature increase rate = 2 °C min<sup>-1</sup>). In a second  
153 step, solution S1 was slowly dropped onto the Zr-SBA support. In both cases, the volume  
154 of solution used for the impregnation corresponded to the pore volume of the powders as  
155 measured by N<sub>2</sub> physisorption. Finally, the solid was dried at 80 °C for 12 h and was  
156 calcined under static air at 700 °C (temperature increase rate = 2 °C min<sup>-1</sup>).

157 *Case of TS procedure:* 2.0 g of the freshly calcined silica (SBA or KIT) were dispersed in  
158 70 mL of pentane (J.T. Baker, analysis reagent, ≥98%,) by stirring during 15 min.  
159 Thereafter, aqueous precursor solution (prepared by dissolving ZrO(CO<sub>3</sub>)·xH<sub>2</sub>O (Amuco  
160 Inc. ≥40% ZrO<sub>2</sub>) in water) was added dropwise to the pentane containing silica. The

161 volume of water added corresponded to 1/2 of the support pore volume as measured by N<sub>2</sub>-  
162 physisorption, in which calculated mass of zirconium precursor was dissolved. The powder  
163 was recovered by filtration, dried at 80 °C for 12 h and calcined under static air at 700 °C  
164 for 1 h (temperature heating rate = 2 °C min<sup>-1</sup>). Step of nickel impregnation was performed  
165 using an exactly similar procedure, dissolving the mass of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma–Aldrich,  
166 ≥98.5%, p.a. grade) in water. For final activation, the catalyst is calcined under static air at  
167 700 °C.

168 The catalysts were named as follow: NiZr-S-IMP, where S indicated the support name  
169 (SBA or KIT) and IMP indicated the selected method of impregnation, TS or IWI.

### 170 **2.3. Preparation of ZrO<sub>2</sub> supported Ni catalyst**

171 Mesoporous ZrO<sub>2</sub> (meso-Zr) was synthesized using nanocasting approach, using SBA-15  
172 silica as hard template [78]. Firstly, the silica powder was dispersed in an excess of organic  
173 solvent (pentane). Secondly, silica porosity was filled with 1.2 mL of an aqueous solution  
174 containing the zirconium precursor, ZrO(CO<sub>3</sub>)·xH<sub>2</sub>O. The resulting mixture was  
175 magnetically stirred for 30 min at room temperature. The powder was recovered by  
176 filtration, air-drying at 80 °C for 24 h, and calcination at 700 °C for 1 h (temperature  
177 heating rate = 2 °C min<sup>-1</sup>). The procedure was repeated a second time in order to increase  
178 zirconia loading. Finally, the silica matrix was removed by dissolution (12 h under stirring),  
179 using a NaOH solution (0.2 M; 10 mL per g of solid), followed by water washing and  
180 drying at 80 °C. The procedure was repeated two times to ensure a >95 wt% silica removal.  
181 Ni/ZrO<sub>2</sub> (Ni/meso-Zr) was prepared using IWI procedure, using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O precursor.  
182 After impregnation, the powder was dried at 90 °C for 12 h, and calcined at 700 °C for 1 h  
183 (temperature heating rate = 2 °C min<sup>-1</sup>).

184 For comparison, a catalyst was prepared using a conventional ZrO<sub>2</sub> support, obtained by  
185 thermal decomposition of the zirconium precursor, ZrO(CO<sub>3</sub>)·xH<sub>2</sub>O, at 700 °C (1 h ;  
186 temperature heating rate = 2 °C min<sup>-1</sup>). The impregnation of nickel precursor solution was  
187 performed using IWI procedure. This catalyst was named as Ni/ZrO<sub>2</sub>.

### 188 **2.4. Characterization methods**



189 Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) was performed to  
190 determine the elemental composition of catalysts (Ni, Zr and Si), using a 720-ES ICP-OES  
191 Agilent instrument with axially viewing and simultaneous CCD detection. The wavelengths  
192 used were: 221.320 nm (Ni), 267.865 nm (Zr) and 198.863 nm (Si). For analysis, a known  
193 mass of catalyst (10.0 mg) was dissolved in 1 mL of concentrated HF solution and 2 mL of  
194 concentrated *aqua regia* solution. The samples were heated up to 110 °C (Vulcan digester).  
195 Then, 4 mL of UNS-1 solution (Inorganic Ventures) were added to deactivate HF and to  
196 maintain solubility of the sample through complexation. Finally, samples were diluted up to  
197 20 mL in water.

198 N<sub>2</sub> adsorption-desorption isotherms were recorded at 77 K on an ASAP2010 instrument  
199 from Micromeritics. Before each analysis, the sample was degassed at 250 °C during 12 h  
200 (residual pressure < 0.00667 mbar). The Brunauer-Emmett-Teller (BET) method was  
201 applied to calculate the specific surface area. The Barrett-Joyner-Halenda (BJH) method  
202 was applied on the adsorption branch to determine the pore size distribution and the mean  
203 pore size value. Total pore volume was estimated on the adsorption branch, at a P/P<sub>0</sub> value  
204 of 0.95.

205 Powder XRD patterns were obtained using a Bruker AXS D8 advanced X-Ray  
206 diffractometer equipped with a CuK $\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) anticathode and a Lynxeye xe-t type  
207 detector (operating at 40 kV and 40 mA). Diffractograms were recorded for  $2\theta$  from 10 to  
208 80°, with steps of 0.02° (step time of 2 min). For low-angle analysis, the diffractograms  
209 were collected in the reflection mode in the  $2\theta$  range from 0.5 to 5° with a step of 0.02°  
210 (step time of 2 s).

211 Morphology of catalysts was evaluated using Scanning Electron Microscopy (SEM), with a  
212 JEOL JSM-6490 LV instrument. For analysis, samples were fixed on a graphite ribbon, and  
213 surface was coated with gold for analysis (using a DENTON VACUUM Desk IV  
214 equipment). The microscope was equipped with an EDX detector, allowing to perform  
215 element mapping on material surface. To determine active phase dispersion, samples were  
216 characterized by Transmission Electron Microscopy (TEM). Images were recorded on a  
217 Tecnai F20 Super Twin TMP instrument. For analysis, samples were embedded in a resin  
218 and cut into ~100 nm width slices using an EM UC7 LEICA ultramicrotome.

219 X-ray Photoelectron Spectroscopy (XPS) was performed over calcined samples, before  
220 reduction step. The spectra were recorded on a KRATOS Analytical AXIS Ultra<sup>DLD</sup>  
221 spectrometer equipped with a charge neutralizer. The analysis was made under an ultrahigh  
222 vacuum of  $\sim 5 \times 10^{-9}$  Torr. X-ray were produced by an aluminium anode operating with Al  
223  $K_{\alpha}$  source (1486.6 eV) at 15 kV. The binding energy (BE) values were referred using the  
224 binding energy peak of Si 2p at 103.5 eV [79]. The surface Zr/Si, Ni/Si, Ni/Zr and Si/O  
225 atomic ratios were calculated using the CASA XPS software, after subtracting a nonlinear  
226 Shirley background.

227 Dihydrogen Temperature Programmed Reduction ( $H_2$ -TPR) analysis was performed on an  
228 AUTOCHEM 2920 Micromeritics analyzer, equipped with a thermal conductivity detector  
229 (TCD). For each experiment, 50 mg of catalyst were pretreated at 400 °C under helium  
230 flowing ( $50 \text{ mL min}^{-1}$ ) for 1 h. Thereafter, the sample was cooled down to 35 °C and heated  
231 under  $H_2$  flow (5.0 vol.%  $H_2$  diluted in Ar, total flow rate of  $50 \text{ mL min}^{-1}$ ) from 40 °C to  
232 900 °C, applying a temperature increase rate of  $10 \text{ °C min}^{-1}$ .  $H_2$  concentration variation is  
233 registered online on the TCD, affording to quantify the extent of material reduction.

234  $NH_3$ -TPD analysis was carried out on a Micromeritics AUTOCHEM 2910 equipment,  
235 equipped with a TCD detector, and coupled with a mass spectrometer for  $NH_3$   
236 quantification. The samples (100.0 mg) were pretreated under He flow ( $30 \text{ mL min}^{-1}$ ) at  
237 400 °C for 1 h, and the samples were cooled down to 35 °C. Thereafter, the samples were  
238 heated under  $H_2$  flow (5.0 vol.%  $H_2$  in Ar, total flow rate =  $50 \text{ mL min}^{-1}$ ) from 40 °C to 450  
239 °C (heating rate of  $10 \text{ °C min}^{-1}$ ). Finally, the solids were exposed to a flow containing 10  
240 vol.%  $NH_3$  in He ( $30 \text{ mL min}^{-1}$ ) for 30 min at 100 °C. The physisorbed ammonia was  
241 purged with He ( $30 \text{ mL min}^{-1}$ ) for 1 h.  $NH_3$  desorption was measured, applying a  
242 temperature increase rate of  $5 \text{ °C min}^{-1}$  up to 700 °C under a He flow ( $30 \text{ mL min}^{-1}$ ). The  
243 temperature is maintained at 700 °C during 1 h to ensure the TCD baseline return to its  
244 initial value. The  $NH_3$  concentration was on line monitored on a Pfeiffer vacuum  
245 OmniStar<sup>TM</sup> GSD301 mass spectrometer, allowing, after integration of the signal, to  
246 determine the total  $NH_3$  amount desorbed during the cycle.

## 247 **2.5. HDO of guaiacol catalytic reaction**

248 Guaiacol catalytic hydrodeoxygenation reaction was performed in a stainless-steel batch  
 249 reactor (OGAWA, 25 mL). Prior to the reaction, the catalysts were reduced at 450 °C for 2  
 250 h (temperature increase rate of 5 °C min<sup>-1</sup>) under H<sub>2</sub> (total flow rate = 50 mL min<sup>-1</sup>).  
 251 Hexadecane is selected as solvent for the reaction, since the use of non-polar solvent  
 252 favored hydrogenation of the aromatic ring by leading to a coplanar adsorption of the  
 253 aromatic ring on the catalyst surface. In polar solvents, the vertical adsorption of the  
 254 reactants through the hydroxyl group is favored [80-82]. The absence of external and  
 255 internal mass transfer limitations was also confirmed in the conditions of reaction applied  
 256 with the solvent selected. The details of the procedure were reported in a previous paper  
 257 [83]. The mass transfer limitations were evaluated using the Weisz-Prater (C\_WP) and  
 258 Mears Criterion (C\_M). The estimated C\_WP and C\_M values were below 1 and 0.15,  
 259 respectively, indicating that internal pore diffusion and external diffusion limitations were  
 260 negligible. To conclude, under selected reaction conditions, the reaction was not controlled  
 261 by diffusional effects.

262 For each experiment, 17.5 mL of guaiacol solution (0.6 mol L<sup>-1</sup>) in hexadecane and 0.1 g of  
 263 catalyst were added into the reactor, which was thereafter sealed and purged under H<sub>2</sub>. The  
 264 reactor temperature was set at 300 °C. When temperature reached 300 °C, stirring rate was  
 265 stabilized at 600 rpm and 5 MPa of H<sub>2</sub> was added into the reactor. Reaction ended after 8 h.  
 266 Liquid products were analyzed using a gas chromatograph (GC, Shimadzu QP2010 Ultra)  
 267 equipped with a flame ionization detector and a DB-5 capillary column (30 m x 0.25 mm x  
 268 0.10 μm) for product separation. Tetradecane was selected as internal standard. Liquid  
 269 samples were also analyzed using mass spectrometry to identify organic compounds  
 270 present.

271 Conversion and product yields were calculated as follow:

272  $Conversion\ of\ guaiacol, C_{GUA}(\%) = \frac{n_{GUA, in} - n_{GUA, out}}{n_{GUA, in}} \times 100;$        $Yield, Y_{product\ i}(\%) =$

273  $\frac{n_{product\ i}}{n_{GUA, in}} \times 100;$  Where  $n_{GUA, in}$  is the initial number of moles of guaiacol,  $n_{GUA, out}$  is

274 the final number of moles of guaiacol,  $n_{product\ i}$  is the number of moles of the i<sup>th</sup> product  
 275 formed in the liquid phase.

276 Carbon balance was calculated as follow:  $Carbon\ balance, C_{balance}(\%) =$

277  $\frac{\sum n_{C, product\ i} + n_{GUA, out}}{n_{GUA, in}} \times 100.$  Where  $\sum n_{C, product\ i}$  is the sum of number of moles of C in

278 each identified product. Gas phase analysis is performed by Gas Chromatography. The  
279 detailed procedure is presented in ESI file.

280 Catalytic tests were performed two times to ensure reproducibility of the results.  
281 Conversion and selectivity presented are the average values of the two tests. The standard  
282 deviation for all reported data is 2%.

### 283 3. Results and discussion

#### 284 3.1. Catalyst composition

285 Catalysts composition was determined using ICP analysis (Table 1). The results showed  
286 that nickel contents vary from 7.7 to 11.0 wt.%, depending on the preparation method. The  
287 experimental Zr loading was measured at values from 10.1 to 11.4 wt.%. Silicon content in  
288 Ni/meso-Zr was also determined, since silicon is a residue from the nanocasting synthesis  
289 to produce the mesoporous zirconia. A value of 1.9 wt.% of Si was determined, indicating  
290 that the approach adopted ensured an almost complete dissolution of the initial silica  
291 template.

292

293 **Table 1.** Catalyst composition and selected textural properties of supports and catalysts.

Sample	Ni content (wt.%)	Zr content (wt.%)	$V_p$ ( $\text{cm}^3 \text{g}^{-1}$ )	$\Delta V_p^a$ (%)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$\Delta S_{\text{BET}}^a$ (%)	$d_{\text{BJH}}$ (nm)
SBA-15	---	---	1.20	---	520	---	11.4
NiZr-SBA-IWI	7.7	10.1	0.82	31	347	33	9.7
NiZr-SBA-TS	11.0	10.6	0.86	28	363	30	9.8
KIT-6	---	---	1.20	---	830	---	6.7
NiZr-KIT-TS	9.7	11.4	0.63	47	462	44	6.2
Meso-Zr	---	---	0.40	---	204	---	4.9; 7.5
Ni/meso-Zr	8.7	---	0.28	30	141	31	4.6; 7.3

294 <sup>a</sup> loss proportion after deposition of the nickel and zirconium phases.

295

#### 296 3.2. Textural and structural characterization

297 The results of nitrogen adsorption-desorption characterization are gathered in Table 1.  
298 Isotherms and pore size distribution are presented in Figure S1. Isotherms for SBA-15,  
299 KIT-6 silica supports, as well as for NiZr-based catalysts, are of type IV (Fig. S1), a shape  
300 characteristic of mesoporous materials [84]. SBA-15 support presented H1 type hysteresis,  
301 with parallel and vertical adsorption and desorption branches. This isotherm is  
302 characteristic of ordered mesoporous supports having narrow pore size distribution and  
303 cylindrical pores. For KIT-6, while the isotherm remains of type IV, the hysteresis shifted  
304 between H1 and H2, H2 being observed for mesoporous materials presenting  
305 interconnected mesopores.

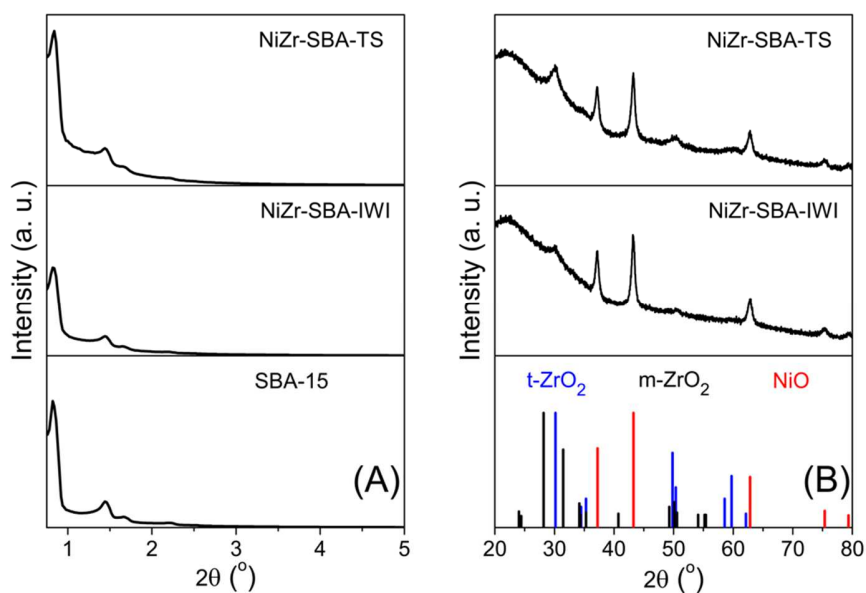
306 After impregnation and calcination for the obtaining of NiO and ZrO<sub>2</sub> supported  
307 nanoparticles, no significant modification of isotherm and hysteresis shapes are observed  
308 (Fig. S1). Proportions of pore volume and surface area decrease after NiO and ZrO<sub>2</sub>  
309 formations are listed in Table 1. Over SBA-15 support, no notable effect of the  
310 impregnation route (TS, IWI) can be noted on the extent of pore volume decrease, which is  
311 for both catalysts around 30%. More important decrease in pore volume was observed over  
312 KIT-6 derived catalyst (47%). For most of the catalysts, the decrease in surface area is  
313 comparable with that of the pore volume: ~ 30% over SBA-15; ~ 44% over KIT-6. Finally,  
314 the limited changes in pore size distribution and mean pore size value (with a maximum of  
315 pore size decrease of 15% in the case of NiZr-SBA materials) is showing a limited  
316 modification of the pore structures upon impregnation - drying - calcination cycle. Results  
317 obtained however suggest that NPs (NiO and ZrO<sub>2</sub>) are formed in the support mesopores,  
318 resulting in a consequent pore filling (reflected by pore volume and surface area decreases,  
319 and a limited pore size change). For meso-Zr and Ni/meso-Zr (Fig. S1), isotherm of type IV  
320 is obtained, with, however, a larger pore size distribution obtained. These results clearly  
321 demonstrate a less periodic mesopore structure on the long-range order in these materials,  
322 as compared with the silica supports. Surface area of 204 m<sup>2</sup> g<sup>-1</sup> is obtained for the meso-  
323 Zr, a value that is decreasing by 31% after impregnation cycle and calcination for NiO  
324 formation. Comparable decrease in pore volume is measured.

325 Low-angle XRD patterns for SBA-15 and NiZr-SBA catalysts are shown in Figure 1. All  
326 diffractograms displayed one main peak located at  $2\theta \sim 0.82^\circ$  and two additional peaks of  
327 lower intensity located at  $2\theta \sim 1.44^\circ$  and  $1.68^\circ$  (Fig. 1A). Identified reflections are ascribed

328 to the (100), (110) and (200) planes of the ordered pore structure of hexagonal symmetry  
 329 (space group  $P6mm$ ) [74]. Results confirm that the impregnation procedures (IWI or TS) do  
 330 not induce any significant alteration of the long-range ordering in the SBA-15 silica, as  
 331 deduced from the maintaining of comparable isotherms shape and hysteresis. Similar  
 332 results were obtained for KIT-6 based materials (Fig. 2A), with diffraction peaks located at  
 333  $2\theta \sim 0.98^\circ$ ,  $1.16^\circ$  and  $1.9^\circ$ , ascribed to the (211), (200) and (332) reflections of the cubic  
 334 structure of  $Ia3d$  symmetry [76]. For meso-Zr and Ni/meso-Zr (Fig. 3A), low-angle  
 335 reflections were poorly defined compared to those recorded over the ordered silica  
 336 containing solids. The main peak, of highest intensity and characteristic of the (100) plan  
 337 was located at  $2\theta \sim 0.88^\circ$ , while a second broad signal was observed at  $1.40^\circ$ . Although  
 338 they were not well resolved, they indicated the formation of a periodic mesoporous  
 339 structure, the broadening of the signal being often observed over non-siliceous oxides  
 340 produced by nanocasting [85, 86].

341

342



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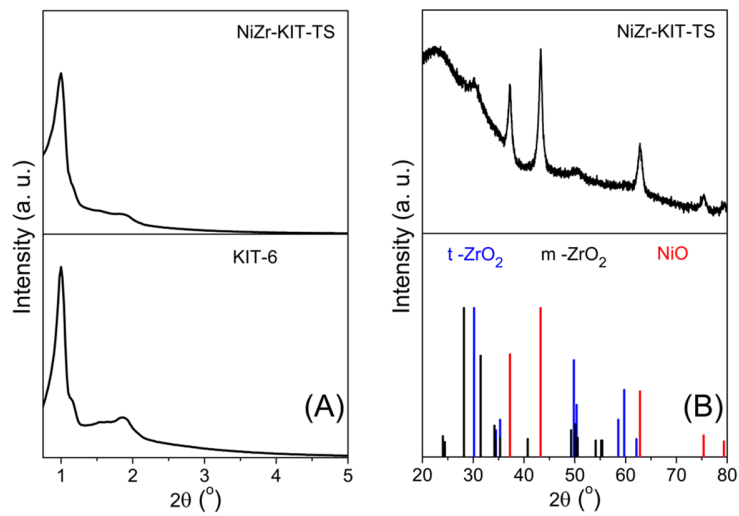
344 **Figure 1.** (A) Low-angle X-ray diffraction patterns for: SBA-15, NiZr-SBA-IWI, NiZr-  
 345 SBA-TS; (B) wide-angle X-ray diffraction patterns for: NiZr-SBA-IWI, NiZr-SBA-TS.

346

347 Diffractograms recorded for  $2\theta$  values between  $20^\circ$  and  $80^\circ$  are presented in Figure 1 to  
348 Figure 3. Reflections located at  $2\theta \sim 30.1^\circ$ ,  $35.1^\circ$ ,  $50.1^\circ$  and  $60.0^\circ$  are characteristic of  
349 tetragonal  $\text{ZrO}_2$  phase (JCPDS file n°17-0923). Only tetragonal phase is observed to form  
350 in materials containing impregnated  $\text{ZrO}_2$  phase, and even over meso-Zr. In nickel  
351 containing solids, additional reflections located at  $2\theta \sim 37.2^\circ$ ,  $43.3^\circ$ ,  $62.9^\circ$ ,  $75.4^\circ$  and  $79.3^\circ$   
352 are observed. These reflections are characteristic of NiO phase (PDF file n°01-073-1523).

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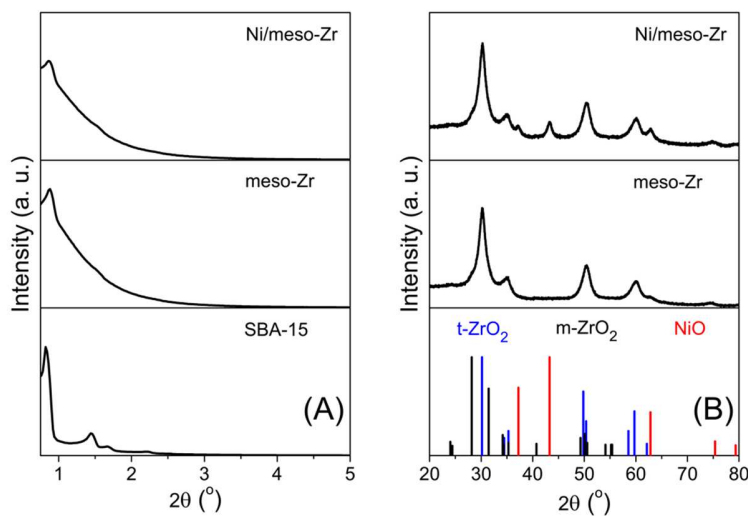
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355

356 **Figure 2.** (A) Low-angle X-ray diffraction patterns for: KIT-6, NiZr-KIT-TS; (B) wide-  
357 angle X-ray diffraction patterns for: NiZr-KIT-TS.

358



359

360 **Figure 3.** (A) Low-angle X-ray diffraction patterns for: SBA-15, meso-Zr, Ni/meso-Zr; (B)  
 361 wide-angle X-ray diffraction patterns for: meso-Zr and Ni/meso-Zr.

362

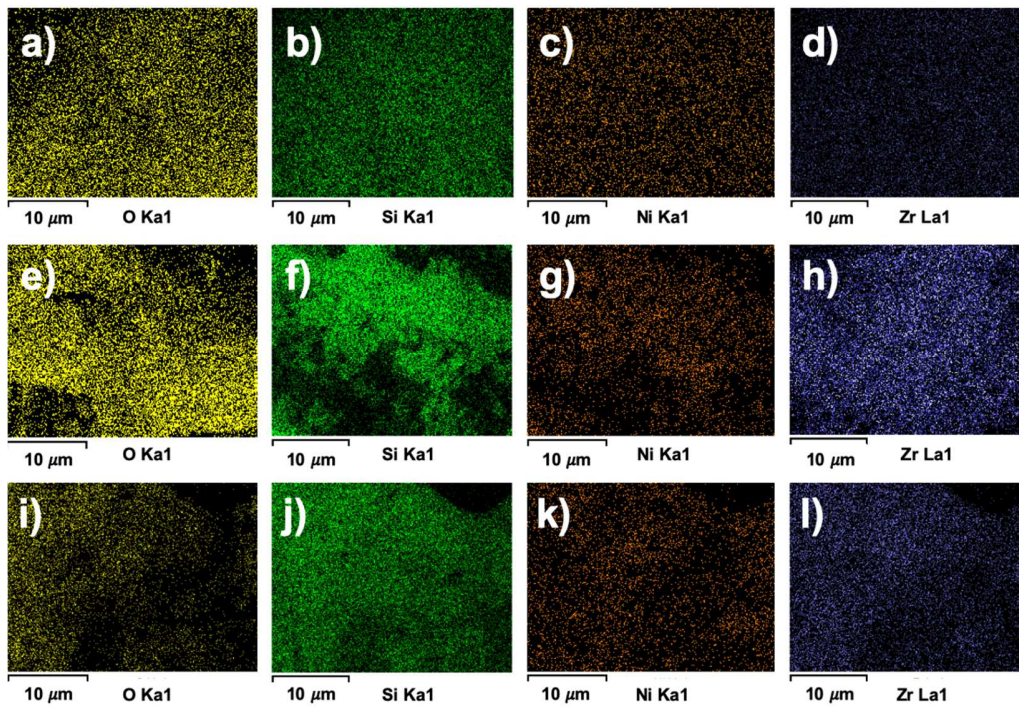
### 363 3.3. Morphology characterization

364 SEM images obtained for Ni-ZrO<sub>2</sub> supported catalysts are shown in Figure S2. For SBA-  
 365 based catalysts (NiZr-SBA-TS in Fig. S2a), silica particles exhibited a rope-like shape  
 366 forming string-like aggregates. This is a classical morphology observed for SBA-15 type  
 367 support [87, 88]. NiZr-KIT-TS (Fig. S2b) showed particles without a defined shape and  
 368 wide-open spaces visible on the surface. Finally, images of the Ni/meso-Zr (Fig. S2c)  
 369 showed characteristic, although not uniform, string-like aggregates, comparable to that of  
 370 the SBA-15 used as hard-template. It indicates that the morphology of the silica template  
 371 determines the morphology of the ZrO<sub>2</sub> particles obtained by nanocasting.

372 Macroscopic dispersion of elements was evaluated by EDX-mapping (Fig. 4 and Fig. 5 for  
 373 calcined catalysts; Fig. 6 for reduced catalyst). No evident segregation of Ni and Zr through  
 374 the whole areas analyzed can be observed. These results indicate a satisfying dispersion of  
 375 elements issued from the impregnation process. For the Ni/meso-Zr catalyst, silicon is also  
 376 detected at low intensity (Fig. 5) in accordance to ICP analysis result confirming the  
 377 presence of residual silica template in the final material. After reduction of NiZr-KIT-TS  
 378 sample (Fig. 6), EDX-mapping showed no significant sintering of the elements, with Si, Zr  
 379 and Ni species always observed to be well-distributed in the whole analyzed areas.

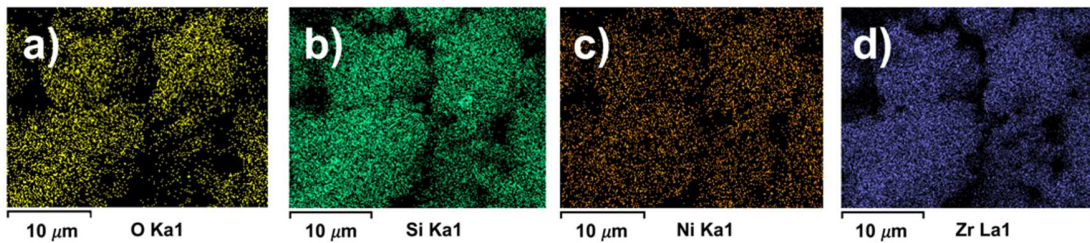


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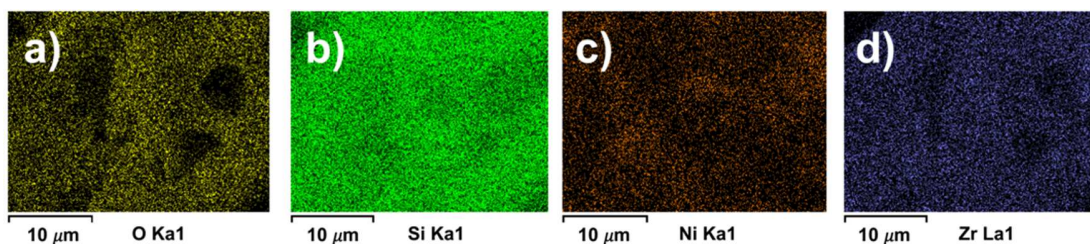
382 **Figure 4.** SEM EDX analyses. Oxygen in yellow, Silicon in green, Nickel in brown and  
383 Zirconium in blue for a-b-c-d) NiZr-SBA-IWI, e-f-g-h) NiZr-SBA-TS and i-j-k-l) NiZr-  
384 KIT-TS.



385

386 **Figure 5.** SEM EDX analyses. Oxygen in yellow, Silicon in green, Nickel in brown and  
387 Zirconium in blue for Ni/meso-Zr.

388



389

390 **Figure 6.** SEM EDX analysis. Oxygen in yellow, Silicon in green, Nickel in brown and  
391 Zirconium in blue for reduced NiZr-KIT-TS sample (450 °C, 2 h).

392

393 Transmission electron microscopy was performed to determine Ni- and Zr-containing  
394 phases localization and size. TEM images obtained for NiZr-SBA and NiZr-KIT catalysts  
395 are presented in Figure 7. Support mesopores of uniform size are clearly observed,  
396 confirming the preservation of the pore structure after impregnation - activation cycle (as  
397 deduced from N<sub>2</sub>-physisorption and low angle XRD experiments). Such retaining of initial  
398 pore structure was observed regardless of the impregnation method (IWI, TS) and silica  
399 support type (SBA, KIT). Then, the observed decrease in textural parameters (Table 1, 30  
400 to 40% of the initial values) can be attributed to pore clogging more than to pore collapse.  
401 Indeed, NiO and/or ZrO<sub>2</sub> nanoparticles were observed to form confined within the pores.  
402 This observation is valid for both IWI and TS-derived catalysts. The presence of a few  
403 proportion of external particles, of larger size (30-50 nm) as visible in Figure 7, was  
404 detected for all impregnated materials and whatever the impregnation route adopted. The  
405 crystalline character of the obtained particles is supported by visible lattice fringes at high  
406 magnification (Fig. 8). The indexation of the diffraction patterns obtained on such  
407 crystallized particles allowed to confirm the presence of tetragonal ZrO<sub>2</sub> (lattice planes  
408 spacing in agreement with JCPDS n°17-0923) and NiO (lattice planes spacing in agreement  
409 with JCPDS n°01-073-1523).

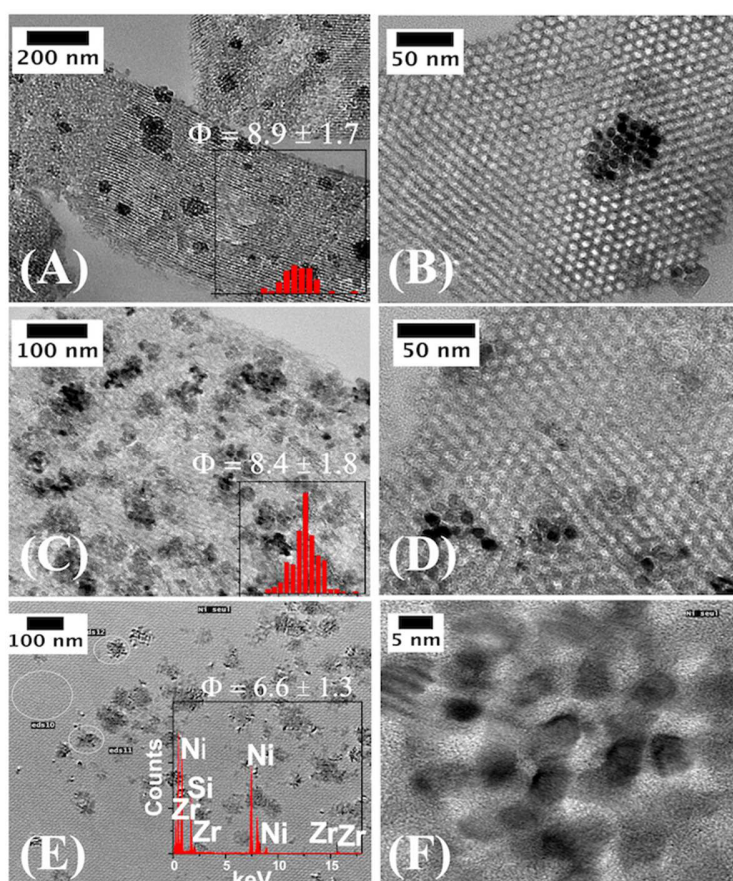
410 The IWI procedure resulted in the formation of mesopore confined nanoparticles (NPs)  
411 with diameter of  $8.9 \pm 1.7$  nm (Fig. 7), a diameter value close to the mesopore diameter of  
412 the parent SBA-15 (Table 1). Formation of NPs assemblies of elementary NPs in the  
413 mesopores, linked together by the connecting secondary pore network of the SBA-15, was  
414 observed, as already reported [89, 90]. Due to the assembly between adjacent mesopores of  
415 several NPs to form pseudo-aggregates of various sizes, some of them exceeding tenths of  
416 nanometers, an inhomogeneous repartition of the impregnated oxides was observed  
417 throughout the silica grain porosity. Focused EDX analysis evidenced formation of Ni-rich  
418 aggregates (from pure nickel) to Zr-rich aggregates (from pure zirconia). However, large-  
419 zone analyses (silica grain scale) showed Ni and Zr loadings close to the expected values.  
420 In the case of the TS approach, formation of mesopore confined NPs (Fig. 7-8) was also



421 observed, but with a reduced size of the assemblies formed between the adjacent mesopores  
422 and a better metal oxide distribution within the mesopores of the support is obtained  
423 (whatever the support morphology, SBA-15 or KIT-6). The average NPs size in NiZr-SBA-  
424 TS reached  $8.4 \pm 1.8$  nm, value close to the mesopore diameter of the parent SBA-15  
425 (Table 1). For NiZr-KIT-TS, average NPs size of  $6.6 \pm 1.3$  nm was obtained, a value in  
426 agreement with the pore diameter of the silica KIT-6 support. To conclude, NiO and ZrO<sub>2</sub>  
427 particles confined in the mesopores of SBA-15 and KIT-6 silica supports form when  
428 catalysts are prepared by the IWI and TS approach. Confining of NPs results in pore  
429 plugging that can explain the evolutions in textural parameters as observed for the surface  
430 area and pore volume evolutions.

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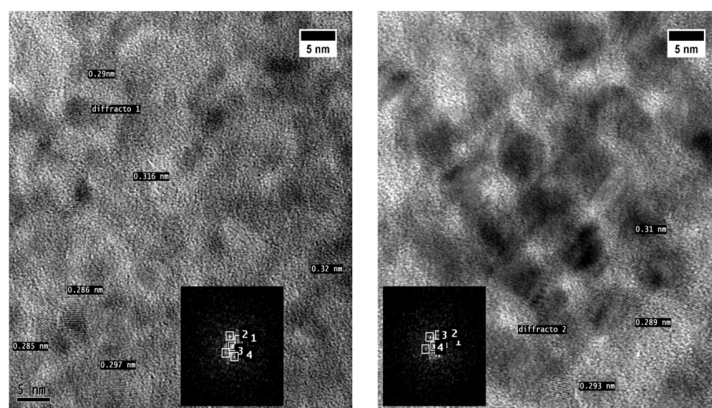
434 **Figure 7.** TEM images obtained for (A, B) NiZr-SBA-IWI, (C, D) NiZr-SBA-TS and (E,  
435 F) NiZr-KIT-TS after calcination at 700 °C.

436

437 Finally, images obtained for Ni/meso-Zr are presented in Figure 9. The formation of porous  
438 ordered material with pseudo-spherical/cylindrical pores of 8-10 nm in size is observed.  
439 The observations fit with the low XRD angle analysis and N<sub>2</sub>-physisorption results since  
440 they described a material with a poor pore ordering. Finally, in this material, NiO NPs of  
441 4.4 ± 1.3 nm average size, aleatory distributed in the ZrO<sub>2</sub> porosity, are observed to form.

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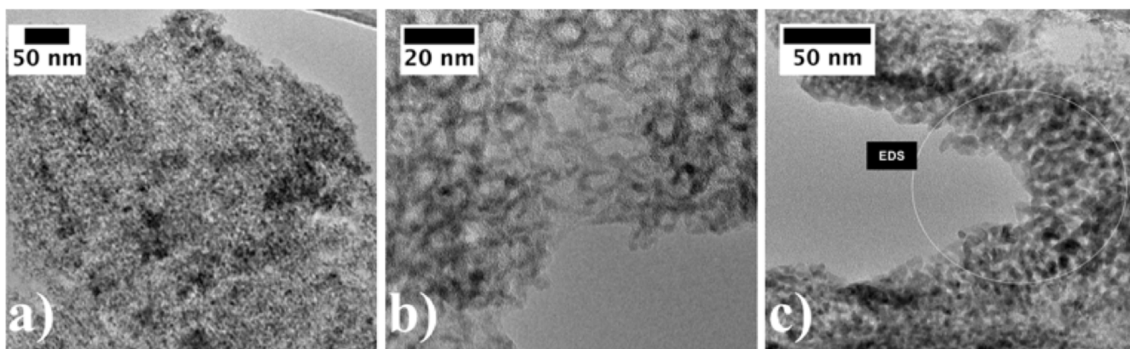
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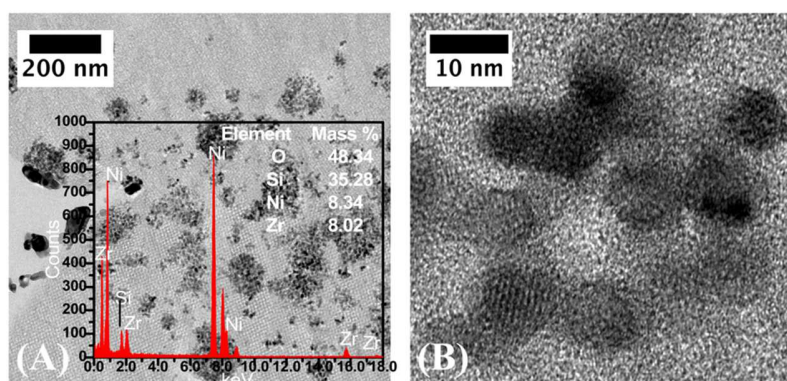
445 **Figure 8.** TEM images of NiZr-KIT-TS sample with particles showing lattice fringes. Fast  
446 Fourier transform (FFT) image is shown (inset).

447



448

449 **Figure 9.** TEM images for Ni/meso-Zr after calcination at 700 °C.



450

451 **Figure 10.** TEM images of NiZr-KIT-TS catalyst after reduction at 450 °C for 2 h.

452 Stability of NPs under reducing atmosphere was evaluated for the NiZr-KIT-TS sample,  
 453 applying a reduction at 450 °C (pure H<sub>2</sub> at a total flow rate = 50 mL min<sup>-1</sup>, heating rate of 5  
 454 °C min<sup>-1</sup>) (Fig. 10). No notable evolution of the mesopore confined NPs size ( $7.2 \pm 1.9$  nm  
 455 for Ni-ZrO<sub>2</sub>) and support morphology could be observed after reduction, with the NPs  
 456 remaining always confined in mesopores and forming aggregates of sizes ranging from few  
 457 tenths of nanometers to one hundred of nanometers. For the external particles, even if few  
 458 in proportion, significant sintering was observed, as shown in Figure 10A, selected to show  
 459 these rarely observed external particles. From a composition point of view, EDX analysis  
 460 revealed the presence of both Ni and ZrO<sub>2</sub> in the particles assemblies of NPs located inside  
 461 the silica pores (>100 nm), as observed before reduction. EDX analysis on isolated particles  
 462 or few particles assemblies revealed the maintaining of Ni to Zr composition heterogeneity  
 463 at the particle level.

#### 464 **3.4. Surface XPS characterization**

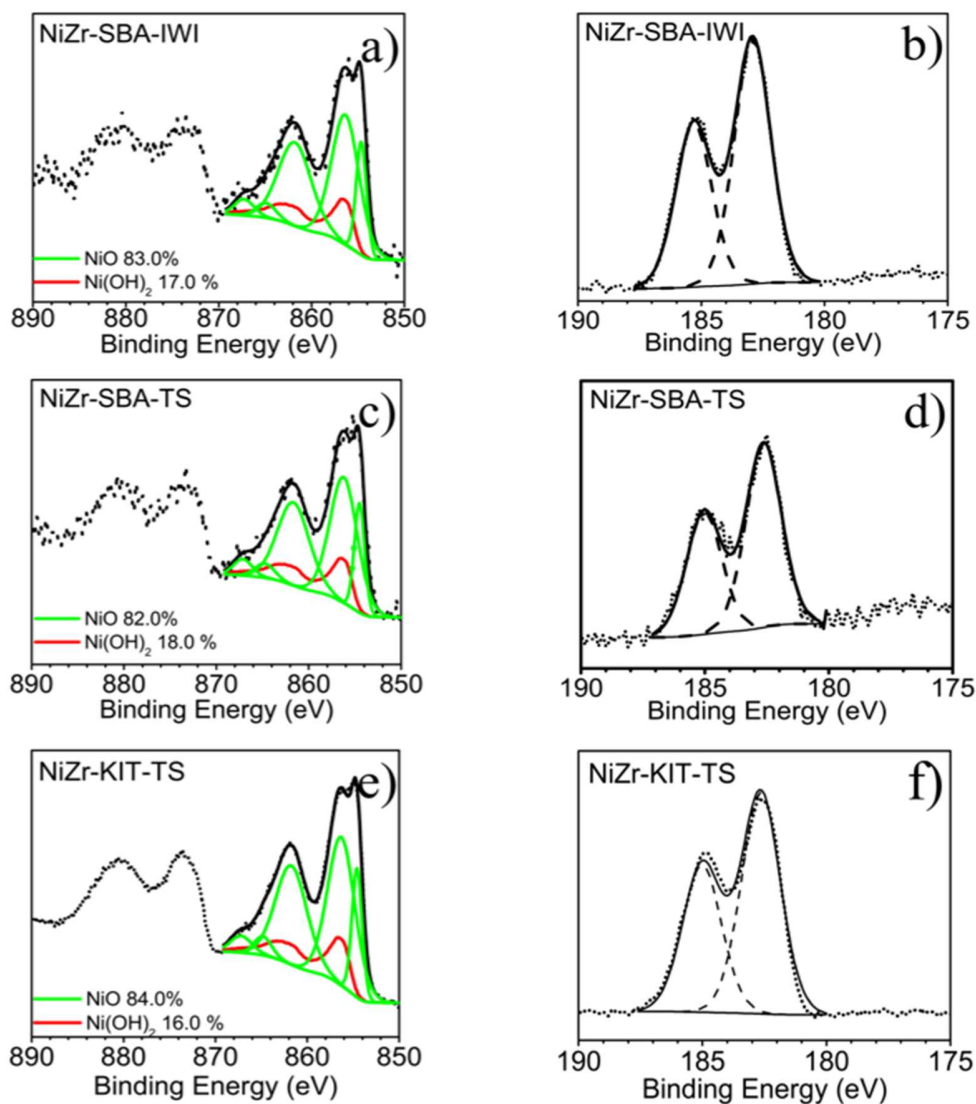
465 XPS analysis was carried out to investigate the chemical state of Ni and Zr on the catalysts  
 466 surface.

467 *Over silica supported catalysts:* the Ni 2p spectra of catalysts (Fig. 11) exhibited a main Ni  
 468 2p<sub>3/2</sub> signal splitting into two components. Values of the binding energy at ~854-856 eV are  
 469 commonly attributed to Ni 2p<sub>3/2</sub> in NiO species. The multiplet splitting of the main signal  
 470 with both maxima being separated from 1.9 eV is also characteristic of NiO formation [91],  
 471 in agreement with the phase identified by XRD. Additionally, the Ni 2p spectra, exhibiting  
 472 signals at  $856.6 \pm 0.1$  eV, indicated the formation of Ni(OH)<sub>2</sub> species [91]. NiO and

473 Ni(OH)<sub>2</sub> species were then both formed on the catalysts surface, with relative compositions  
474 of NiO in the range 82-84% and Ni(OH)<sub>2</sub> in the range 16-18%, independently of the silica  
475 support or the impregnation route. The Zr 3d spectra (Fig. 11) showed the doublet peaks of  
476 Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> located at 182.0-182.9 eV and 184.9-185.6 eV, respectively. Binding  
477 energies at 182.4 eV and 185.3 eV are commonly reported for Zr in IV oxidation state [92].  
478 Then, the results obtained suggested the exclusive presence of Zr(IV) species in the  
479 catalysts independently of the silica support type and impregnation route.

480 *Over zirconia catalysts:* Ni 2p spectra also indicated the presence of NiO and Ni(OH)<sub>2</sub>  
481 species (Fig. 12), with Ni(OH)<sub>2</sub> being the main species (~65%) and NiO the secondary  
482 species (~35%). These results demonstrated a higher reactivity of NiO toward  
483 rehydroxylation when supported over pure ZrO<sub>2</sub> than over SiO<sub>2</sub>. Zr 3d spectra (Fig.12), as  
484 for the three silica supported catalysts, indicated the presence of only Zr(IV) species [92,  
485 93]. Finally, for this sample, silicon was also quantified by XPS and, as observed by ICP,  
486 Si was detected at a concentration of 9.5 at.%. For instance, this result confirmed that the  
487 silica hard-template was not completely removed upon NaOH dissolution step.

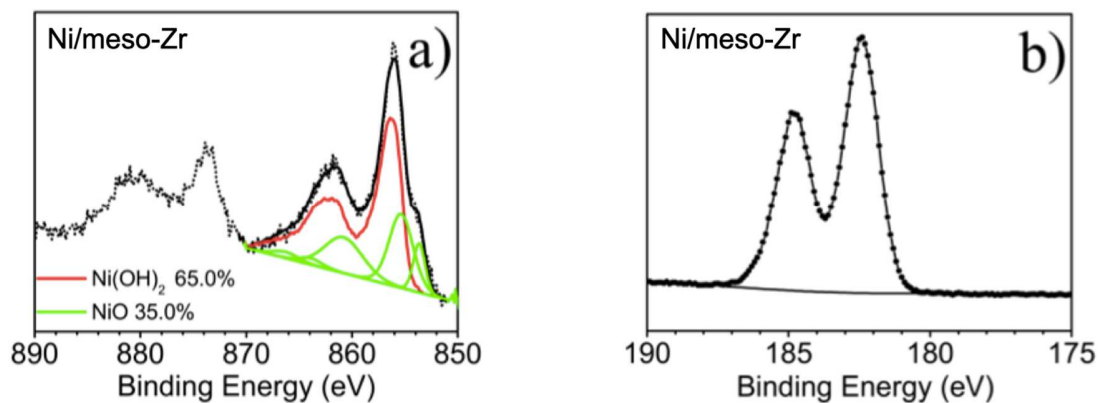
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490

491 **Figure 11.** XPS Ni 2p spectra for a) NiZr-SBA-IWI, c) NiZr-SBA-TS, e) NiZr-KIT-TS;

492 and XPS Zr 3d spectra for b) NiZr-SBA-IWI, d) NiZr-SBA-TS, f) NiZr-KIT-TS.



493

494 **Figure 12.** a) XPS Ni 2p spectrum and b) XPS Zr 3d spectrum for Ni/meso-Zr.

495

### 496 3.5. Temperature-programmed reduction (H<sub>2</sub>-TPR)

497 NiO reducibility was determined by TPR (Fig. 13). Both NiZr-SBA-IWI and NiZr-SBA-TS  
498 samples showed a major hydrogen consumption located between 370-395 °C and a minor  
499 one located between 492-520 °C. NiZr-KIT-TS sample exhibited hydrogen consumptions  
500 at slightly higher temperatures, centered at 413 °C and 507 °C.

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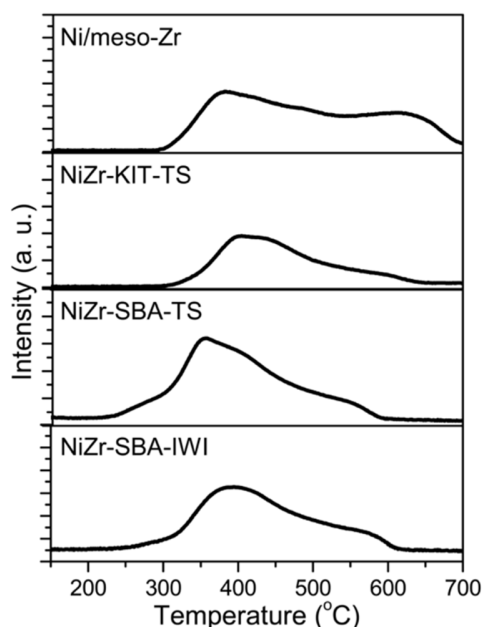
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514 **Figure 13.** Temperature-programmed reduction of NiZr-silica and Ni/meso-Zr samples,  
515 after thermal stabilization at 700 °C.

516 Slight differences in reduction temperature can be related to different dispersion degrees, or  
517 to the presence of Ni(II) species interacting at different level with SiO<sub>2</sub> surface [94], or  
518 even, in our case to Ni(II) interacting with ZrO<sub>2</sub> phase. For instance, the consumptions  
519 located at T < 500 °C can be associated to large NiO particles poorly interacting with the  
520 support surface and behaving like bulk NiO, while the minor consumptions observed at T >  
521 500 °C are associated to the reduction of smaller NiO particles or ionic nickel (Ni(II) ions)  
522 in strong interaction with the SiO<sub>2</sub>/ZrO<sub>2</sub> surfaces [65, 90, 95]. In the case of Ni/meso-Zr  
523 sample, differences with silica-based catalysts are: (i) the shift of the second reduction peak



524 toward higher temperatures (up to a maximum centered at 616 °C); (ii) the increase of this  
 525 second peak intensity. Such evolution shows that the proportion of small NiO NPs / NiO in  
 526 strong interaction with the support is higher in Ni/meso-Zr than in silica containing  
 527 catalysts. The presence of zirconia phase seems to allow a better stabilization of the nickel  
 528 ionic species, as already reported [96].

### 529 **3.6. Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD)**

530 Acidity of catalysts reduced at 450 °C was measured by NH<sub>3</sub>-TPD (Fig. S3). The values of  
 531 total acidity of catalysts are gathered in Table 2. The strength of the acidic sites is assigned  
 532 according to the desorption temperatures [97-99]: (i) weak acidity, with temperature of  
 533 desorption in the <250 °C range; (ii) medium acidity, with desorption between 250 and 400  
 534 °C and (iii) strong acidity, for temperature of desorption >400 °C.

535 Desorption profiles obtained for silica supported catalysts exhibited two desorption steps  
 536 (Fig. S3a). The first desorption occurred in the temperature range of 150-400 °C, which  
 537 characterizes solids of weak to medium acidity strength. Ammonia adsorbed from Lewis  
 538 acid sites of the tetragonal zirconia are proposed to desorb at comparable temperature [94].  
 539 The second desorption, of lowest intensity, occurred in the 450-700 °C temperature range,  
 540 showing the presence of a small proportion of strong acid sites. Ni/SiO<sub>2</sub> powders were not  
 541 presenting such strong acidity, ammonia being observed to desorb from only weak acid  
 542 sites (at temperatures below 200 °C), while Ni/ZrO<sub>2</sub> exhibited both weak and strong acid  
 543 sites [18]. Coordinatively unsaturated sites formed on ionic nickel phase, and acting as  
 544 Lewis sites of medium strength, can also contribute to the total acidity [97]. However, as  
 545 catalysts were reduced at 400 °C before NH<sub>3</sub>-TPD experiments, acidity is expected to  
 546 mostly originate from Lewis sites from ZrO<sub>2</sub> surface [100, 101].

547 **Table 2.** Amounts of desorbed NH<sub>3</sub> and surface-normalized quantity obtained for the  
 548 reduced catalysts (quantification performed using the m/z = 15 signal).

Sample	Quantity of NH <sub>3</sub> desorbed (μmol g <sup>-1</sup> )	Surface normalized NH <sub>3</sub> quantity (μmol m <sup>-2</sup> )
NiZr-SBA-IWI	131	0.37
NiZr-SBA-TS	144	0.39
NiZr-KIT-TS	164	0.37

meso-Zr	81	0.40
Ni/meso-Zr	148	1.1

---

549

550

551 For meso-Zr (Fig. S3b), a two-step desorption profile was also observed, as in the case of  
552 silica-based catalysts: (i) first desorption from weak to medium acid sites; (ii) second  
553 desorption from strong acid sites. The second peak locates at comparable temperature than  
554 the high temperature desorption obtained on the silica-based catalysts, supporting that the  
555 strong acidity originates well from Lewis sites from the ZrO<sub>2</sub> surface. Ni/meso-Zr  
556 presented comparable two-step desorption, with a shift of the second desorption peak  
557 toward lower temperature by 148 °C. The quantity of ammonia desorbed was multiplied by  
558 a factor of 1.8 between meso-Zr and Ni/meso-Zr (Table 2). Then, the nickel phase  
559 contributes to the global acidity of the material, for the low/intermediate strength acidity,  
560 despite the catalyst was reduced. However, considering that 450 °C is not enough high to  
561 achieve a complete reduction of NiO (Fig. 13), nickel oxidized species acting as Lewis acid  
562 sites remained on the meso-ZrO<sub>2</sub> support.

563 The total acidity of catalysts followed the order NiZr-KIT-TS > Ni/meso-Zr > NiZr-SBA-  
564 TS > NiZr-SBA-IWI, with a difference of only 25% in the total amount of ammonia  
565 desorbed between the less acidic catalyst (NiZr-SBA-IWI) and the more acidic catalyst  
566 (NiZr-KIT-TS). Zirconia phase being more acidic than silica [102], the significant acidity  
567 generated in the silica composites is associated to the efficient dispersion of the ZrO<sub>2</sub> phase  
568 on the mesostructured silica supports. Despite a low loading in ZrO<sub>2</sub>, the consequent  
569 surface generated by the dispersed phase of zirconia contributed to the acidity, which  
570 comes in addition to weak to medium acidity of silica. When normalized per surface unit,  
571 difference in acidity between ZrO<sub>2</sub> and SiO<sub>2</sub> catalysts becomes visible (Table 2):

- 572 - All silica supported Ni-ZrO<sub>2</sub> catalysts presented desorbed quantity of 0.38±0.1 μmol m<sup>-2</sup>.  
573 Neither the support type (SBA-15 or KIT-6) nor the impregnation route (IWI or TS) has  
574 a significant effect on the material acidity;
- 575 - Ni/meso-ZrO<sub>2</sub> catalyst presented a 2.8 times higher acidity, with 1.10 μmol m<sup>-2</sup> NH<sub>3</sub>  
576 desorbed.




### 577 3.7. Catalytic performance in HDO of guaiacol

578 **3.7.1. Activity of catalysts**

579 Before reaction, all catalysts were reduced at 450 °C. As a common result of catalytic tests,  
 580 analysis of the gas phase indicated the formation of CH<sub>4</sub>. Methanol already observed to  
 581 form in previous studies [103] was not detected. Gibbs free energies for reactions of  
 582 methane and methanol production suggest a favored formation of methane (see ESI file,  
 583 section devoted to gas phase analysis). Preliminary tests, performed without catalyst at 300  
 584 °C under 5 MPa of H<sub>2</sub>, demonstrated a 4% guaiacol (GUA) conversion without detection of  
 585 identified reaction products presented in Table 3 (cyclohexane, cyclohexanol and  
 586 methoxycyclohexanol). Below, results of the analysis of the liquid phase are presented and  
 587 results of the analysis of the gas phase are presented in the supporting information.

588

589 **Table 3.** Catalytic properties of silica and zirconia-based nickel catalysts in the guaiacol  
 590 HDO reaction (time of reaction = 8 h, reaction performed at 300 °C under 5 MPa of H<sub>2</sub>).

Catalyst	C <sub>GUA</sub> (%) <sup>*</sup>	Product yield (%)				C <sub>balance</sub> (%)
					Other	
<b>SBA-15</b>	34	0	0	0	0	90.8
<b>KIT-6</b>	24	0	0	0	0	90.0
<b>NiZr-SBA-IWI</b>	47	5.2	0.7	2.3	29.5	94.5
<b>NiZr-SBA-TS</b>	88	63.5	3.9	0.0	10.6	90.0
<b>NiZr-KIT-TS</b>	93	71.6	3.7	1.6	5.6	89.4
<b>Ni/meso-Zr</b>	100	7.8	43.0	18.0	2.8	71.6
<b>Ni/ZrO<sub>2</sub></b>	86	1.6	40.0	19.9	4.2	79.6

591

592 *Case of silica supported catalysts:* Preliminary experiments performed with silica alone,  
 593 SBA-15 and KIT-6, showed GUA conversion of 34% and 24%, respectively. However, no  
 594 products among those listed in Table 3 can be detected. TG-DSC analysis performed over  
 595 SBA-15 after test showed a carbon total weight loss of 15 wt.% (exothermic decomposition  
 596 in the 180-600 °C temperature range). Then, no HDO occurs over silica alone and  
 597 consumption of GUA is only related to side reactions and to organic matter accumulation  
 598 on the silica surface. With silica supported Ni-ZrO<sub>2</sub> catalysts, under the selected conditions  
 599 of temperature and pressure, carbon balances ≥ 89% are always obtained (Table 3),

600 indicating that formation of sub-products through side reactions becomes limited. When  
601 reaction is performed with NiZr-SBA-IWI catalyst, GUA conversion of 47% with a yield  
602 toward cyclohexane of 5.2% is obtained. Major reaction products remain oxygenated  
603 molecules: 1-methyl-1,2-cyclohexanediol, cyclohexanone and methoxycyclohexanone,  
604 listed in the 'other' column in Table 3. Significant higher conversion is obtained with the  
605 NiZr-SBA-TS catalyst, with GUA conversion reaching 88%. In addition, yield to  
606 cyclohexane significantly increased, reaching 63.5% (Table 3). Improvement of yield  
607 toward deoxygenated and hydrogenated product demonstrates the better activity of TS-  
608 derived catalyst for C-O bond cleavage and C=C/C=O bond hydrogenation. Using 3D KIT-  
609 6 support (NiZr-KIT-TS) instead of 2D SBA-15 (NiZr-SBA-TS) allowed to reach slightly  
610 higher GUA conversion, 93%, with yield toward cyclohexane reaching 71.6%.  
611 Consequently, TS method is far more appropriate to prepare efficient HDO catalyst, since  
612 the approach favor the formation of ZrO<sub>2</sub> and Ni particles confined inside the porous hosts.  
613 Confining induces an improved proximity between Ni and ZrO<sub>2</sub> surface, both sites in close  
614 proximity being necessary for achieving a high selectivity into deoxygenated products  
615 during reaction [83, 97, 103]. Acidic properties seem however less important than  
616 proximity between the two phases since large differences in HDO efficiencies are obtained  
617 between IWI and TS derived catalysts while the global acidity/surface acid site density, as  
618 determined by NH<sub>3</sub>-TPD, are comparable (Table 2, Fig. S3). Finally, the 3D mesopore  
619 structure present in the KIT-6 support is expected to be favorable for the diffusion of  
620 reactants/products inside the catalyst, which is reflected by a higher reaction rate than using  
621 SBA-15, with no alteration of the yield into deoxygenated molecules.

622 *Case of zirconia supported catalysts:* Using Ni/meso-Zr catalyst, total conversion of GUA  
623 was obtained after 8 h of reaction (300 °C, 5 MPa H<sub>2</sub>), showing that the catalyst is active. A  
624 catalyst of comparable Ni loading prepared over conventional ZrO<sub>2</sub>, listed as Ni/ZrO<sub>2</sub> in  
625 Table 3, showed lower conversion (86%, Table 3). It demonstrates the beneficial effect of  
626 the porosity developed in the meso-Zr support on the Ni dispersion. As compared with  
627 SiO<sub>2</sub>-supported catalysts, ZrO<sub>2</sub>-supported catalysts were significantly less efficient for the  
628 complete deoxygenation of GUA. Main products formed were cyclohexanol (~40% yields)  
629 and methoxycyclohexanol (~20% yields), while the SiO<sub>2</sub>-supported catalysts afforded the  
630 production of cyclohexane with yields reaching 71.6% in the best case (Table 3). In

631 addition, incomplete carbon balance is obtained, of only 71.6% with Ni/meso-Zr and 79.6%  
632 with Ni/ZrO<sub>2</sub>, suggesting the accumulation of polymerization products / coke on the  
633 catalyst surface during the reaction. This hypothesis was confirmed performing a TG-DSC  
634 analysis over Ni/meso-Zr after 8 h reaction. The results showed a total weight loss of 24.9  
635 wt.% in the temperature range of 100-600 °C (Fig. S4), with a step of organic matter  
636 decomposition accounting for 12 wt.% at ~300°C. The more important accumulation of  
637 carbon species over ZrO<sub>2</sub> support can be associated to its higher surface acidity [104] than  
638 that of silica (only ~6 wt.% loss during the decomposition step is observed for SBA-15  
639 supported catalyst). A two times higher surface acid site density was indeed measured by  
640 NH<sub>3</sub> adsorption (Table 2).

641 Then, the comparison between Ni catalysts supported over ZrO<sub>2</sub> and Ni-ZrO<sub>2</sub> catalysts  
642 supported over silica demonstrated the importance of maintaining a high level of dispersion  
643 of the zirconia phase to obtain high yields in cyclohexane. Ni however remains active for  
644 hydrogenation no matter its environment (supported over silica or over zirconia). On the  
645 contrary, bulk ZrO<sub>2</sub> as support for nickel promoted the formation of hydrogenated and  
646 partially deoxygenated molecules: high yield to cyclohexanol was obtained (~40%), and  
647 side reactions are promoted (with a carbon balance of ~70-80%). When ZrO<sub>2</sub> remains in a  
648 divided state over SiO<sub>2</sub>, confined in the mesopores and in close proximity of Ni NPs,  
649 catalyst becomes more efficient for complete deoxygenation of GUA: 60-70% yields to  
650 cyclohexane is obtained with ~90% carbon balance. Proximity between Ni NPs and ZrO<sub>2</sub>  
651 NPs is consequently a key parameter to maximize hydrodeoxygenation degree of GUA, as  
652 already observed for other molecules [18, 83, 97].

653 The presence of metal particles nearby to defect sites of zirconia surface has been suggested  
654 to catalyze both deoxygenation and hydrogenation reactions [21, 35, 38]. Cyclohexane  
655 formation involves hydrogenolysis of C-O bonds, C=C hydrogenation, and C=O  
656 hydrogenation followed by dehydration. Adsorption that occurs on the oxophilic or acidic  
657 sites with a flat adsorption configuration could be in favor of the C=C/C=O bond  
658 hydrogenation on the metallic sites as well as activation of C-O bond. Results of NH<sub>3</sub>-TPD  
659 (Table 2) probing only the total acidity of the catalyst, do not allow to confirm this  
660 interpretation: Ni/meso-Zr exhibiting the highest density of Lewis acid sites (Table 2) is  
661 less efficient for C-O bond cleavage, high yields in cyclohexanol (~40%) and

662 methoxycyclohexanol (~20%) being obtained. Consequently, there is no direct correlation  
 663 between the quantity of acidic sites and HDO efficiency, as already observed [18, 105] and  
 664 a cooperation between silanol groups on SiO<sub>2</sub> and sites located on ZrO<sub>2</sub> could favor a  
 665 proper flat adsorption of GUA and its intermediates for activation of the C-O bonds and  
 666 hydrogenation of C=C/C=O bonds.

667 Table 4 presents some key results on the GUA HDO over transition metal-based catalysts.  
 668 The catalytic results presented in this work using silica-based supports are among the best  
 669 reported for nickel catalysts, especially considering that most interesting results from Table  
 670 4 are obtained for Ni-doped catalysts (e.g. NiFe, NiCu based formulations). Metallic nickel  
 671 combined with finely divided ZrO<sub>2</sub> on a mesoporous support, especially with a 3D  
 672 mesoporous structure, then afford high selectivity in cyclohexane.

673

674 **Table 4.** Catalytic performance of different Ni-, Cu-, Co-, Fe-, Mo-, and ZrO<sub>2</sub>-based  
 675 catalysts for HDO of guaiacol.

Catalyst	Catalyst amount	Metal loading	[GUA]	P	T (°C)	t (h)	X <sub>GUA</sub> (%)	Cycl.	Meth.	Cyc-ol	Ref.
NiCu/ZrO <sub>2</sub> -SiO <sub>2</sub>	1.5 g	Cu: 5 wt.% Ni: 15 wt.%	10 g/100 g solvent	5MPa/H <sub>2</sub>	300	8	100	S=80.8	---	---	[96]
Ni/HZSM-5	0.05 g	15 wt.%	0.28 mol/L	5MPa/H <sub>2</sub>	250	4	100	Y=79	0	0	[106]
Ni/HZSM-5	0.05 g	20 wt%	1 g	30bar/H <sub>2</sub>	200	2	17.8	---	Y=3.1	Y=3.8	[107]
Ni/CNT	200 mg	15 wt.%	0.232 mol/L	5MPa/H <sub>2</sub>	300	4	100	Y=45	Y=5.8	Y=33.3	[108]
Ni&ZrO <sub>2</sub>	0.25 g	---	1.2 g/25 mL	4MPa/H <sub>2</sub>	300	4	82	Y=44	---	Y=70	[109]
NiCo/Al <sub>2</sub> O <sub>3</sub>	2 wt.%	Ni: 10 wt.% Co:10 wt.%	5 g/45 g solvent	5MPa/H <sub>2</sub>	200	8	96	Y=0.35	---	Y=68.1	[110]
Ni <sub>5</sub> -Fe <sub>1</sub> /CNT	100 mg	total 6.59 wt%	WLHSV=60 h <sup>-1</sup>	3MPa/H <sub>2</sub>	300	---	96.8	S=83.4	---	S=12.7	[111]
NiMo/SBA-15	2 g	NiO: 6 wt% MoO <sub>3</sub> : 30 wt%	40 g (3wt.%)	5MPa/H <sub>2</sub>	250	3	90	S=55.8	S=6.7	S=6.3	[112]
Ni/SiO <sub>2</sub> -ZrO <sub>2</sub>	1.5 g	---	10 g/100 g solvent	5MPa/H <sub>2</sub>	300	8	100	S=96.8	---	---	[113]
Ni/SiO <sub>2</sub> + β(12.5)	50 mg + 50 mg	---	0.10 g/10 mL solvent	3MPa/H <sub>2</sub>	140	5	>99	Y=55.6	Y=29.7	Y=0.8	[114]
Ni/SiO <sub>2</sub> + Hβ(50)	50 mg + 50 mg	---	0.10 g/10 mL solvent	3MPa/H <sub>2</sub>	140	2.5	>99	Y=91.7	---	---	[114]
NiZr-1/CMK-3	0.1 g	Ni: 9.2 wt% Zr: 15.9 wt%	0.6 mol/L	5MPa/H <sub>2</sub>	300	8	100	S=30.3	S=16.4	S=47.9	[83]
NiZr-SBA-TS	0.1 g	Ni: 11.0 wt% Zr: 10.6 wt%	0.6 mol/L	5MPa/H <sub>2</sub>	300	8	88	Y=63.5	Y=0.0	Y=3.9	a
NiZr-KIT-TS	0.1 g	Ni: 9.7 wt% Zr: 11.4 wt%	0.6 mol/L	5MPa/H <sub>2</sub>	300	8	93	Y=71.6	Y=1.6	Y=3.7	a

676

a. This work

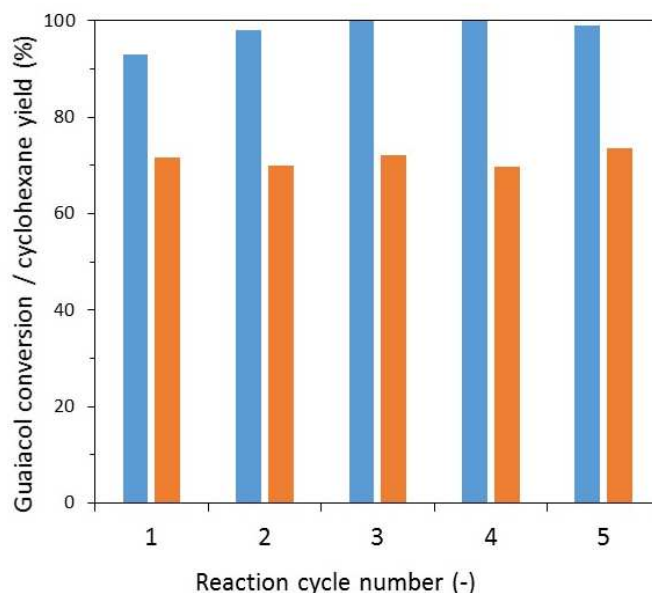
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Cycl.: cyclohexane, Meth.: methoxycyclohexanol, Cyc-ol.: cyclohexanol, Y: yield (%), S: selectivity (%)

678

### 679 3.7.2. Stability of catalysts

680 Stability of catalyst was evaluated by recyclability tests performed over NiZr-KIT-TS (Fig.  
681 14).



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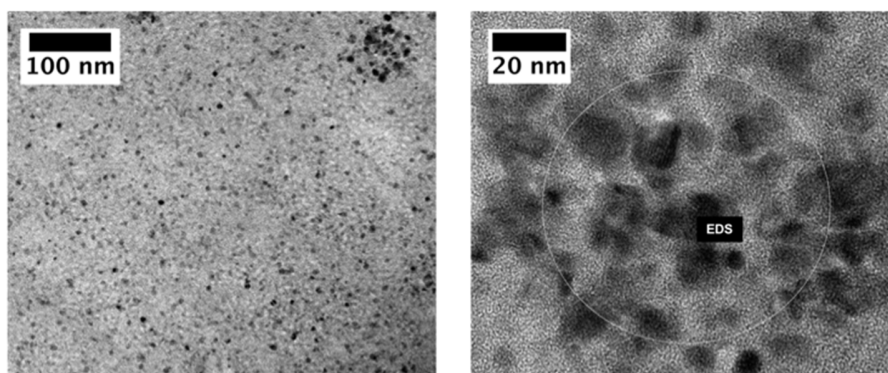
683 **Figure 14.** Recyclability tests performed with NiZr-KIT-TS catalyst (reaction performed at  
684 300 °C for 8 h). Blue bars: guaiacol conversion; Orange bars: cyclohexane yields

685

686 Between two cycles, the catalyst was recovered by filtration before being washed with  
687 acetone and hexane, dried at 100 °C for 12 h. After recovery of the catalyst, a calcination  
688 step is applied in order to remove all adsorbed molecules from the surface (700 °C during 1  
689 h). The catalyst is thereafter reduced at 450 °C, and the mass of GUA was adjusted to the  
690 mass of the catalyst recovered, without modifying the volume of the solvent, for keeping  
691 constant the GUA/catalyst ratio. Results evidenced a satisfying stability, with conversion  
692 observed to slightly increase (from 93% to >98%). Minor variations in cyclohexane yield  
693 are observed between the successive cycles, oscillating at  $70\pm 3\%$ , confirming the absence  
694 of significant deactivation of catalyst. The stability of the catalyst structure was confirmed  
695 by post-reaction characterization (Fig. 15 left). The TEM analysis allowed to observe the  
696 well-defined pore structure of the silica support. Then, silica porosity is not significantly  
697 modified by the reaction and reactivation procedure. In addition, the active phase remains

698 in the form of confined nanoparticles, mostly located inside the mesopores, with particle  
699 size close to those obtained before reaction. Only very few external particle aggregates  
700 were found, and even on these external aggregates (Fig. 15 right) the particles remained of  
701 low size (<20 nm). On the basis of these observations, and with the maintaining of high and  
702 comparable yield in cyclohexane during successive cycles, limited changes in Ni and ZrO<sub>2</sub>  
703 dispersion and proximity are awaited between successive cycles.

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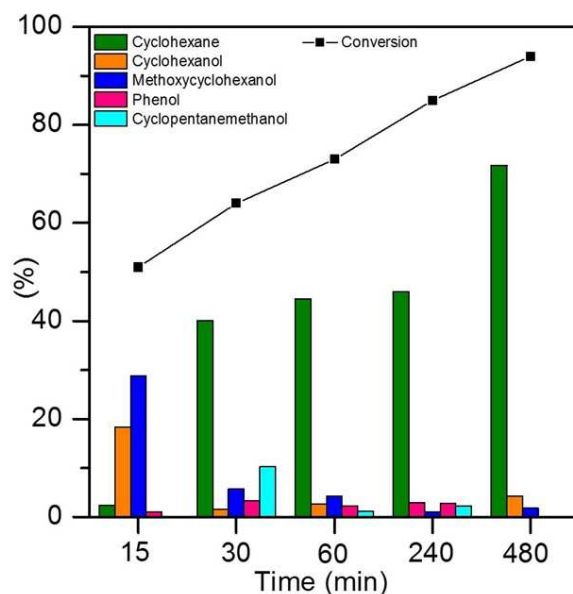
709 **Figure 15.** TEM images of NiZr-KIT-TS catalyst recovered after the 5<sup>th</sup> catalytic cycle,  
710 calcined at 700 °C and further reduced at 450 °C for 2 h.

711

### 712 3.7.3. Conversion route description

713 Evolution of conversion and product yields with reaction time is presented for NiZr-KIT-  
714 TS catalyst in Figure 16. After 15 min of reaction, conversion of GUA reached 51% with a  
715 28.8% yield toward methoxycyclohexanol. Lower yields in cyclohexanol and cyclohexane,  
716 of 18.3% and 2.4% respectively, are obtained. The main products formed are consequently  
717 hydrogenated molecules, indicating as previously described, that Ni is an excellent  
718 hydrogenation catalyst. After 30 min reaction, GUA conversion reached 64% and the yields  
719 underwent significant changes since the main product formed becomes cyclohexane with a  
720 40.1% yield. Secondary products were cyclopentanemethanol, methoxycyclohexanol and  
721 cyclohexanol with yields of 10.3 %, 5.8% and 1.5%, respectively. Gradually increasing the  
722 reaction time to 8 h leads to an increase in GUA conversion, to reach 94%, and with  
723 cyclohexane yield increasing to 71.6% at the expense of the partially deoxygenated  
724 products. The presence of cyclohexane, and the absence of aromatics (benzene) detection is  
725 showing that dehydrogenation reactions are not favored under the reaction conditions  
726 (intermediate temperature of 300 °C and high hydrogen pressure of 5 MPa).





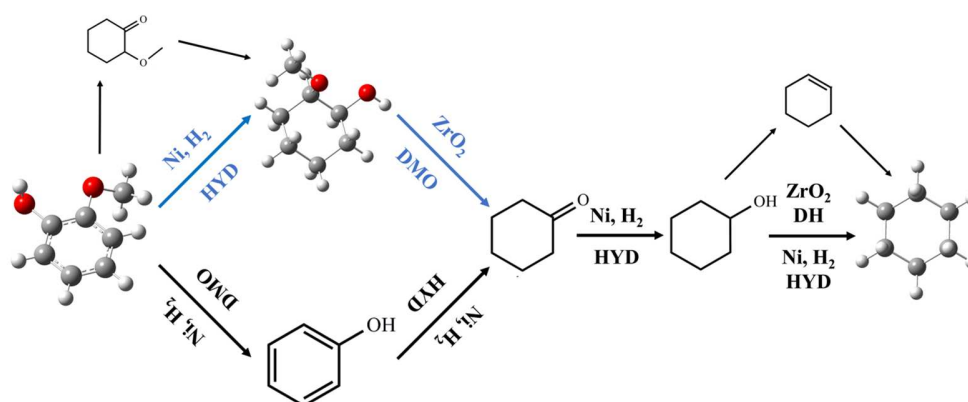
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728 **Figure 16.** Evolution of conversion and product yields with reaction time over NiZr-KIT-  
 729 TS catalyst (reaction performed at 300 °C).

730

731 As observed in Figure 16 at low reaction time, GUA conversion leads to oxygenated  
 732 intermediates, prior to the formation of cyclohexane. In order to better elucidate the  
 733 primary products of the reaction, reaction was performed decreasing the amount of catalyst  
 734 (to 20 mg) and increasing the concentration of GUA (up to 15 wt.%), keeping constant the  
 735 other reaction parameters. Products of the reaction were evaluated at 5 and 10 min reaction  
 736 time. After 5 min of reaction under these modified conditions, limited GUA conversion is  
 737 obtained (16%) and the main products formed were methoxycyclohexanol, phenol,  
 738 cyclohexanol and cyclohexanone with 7.0%, 5.6%, 1.6% and 1.0% yields, respectively.  
 739 After 10 min reaction, GUA conversion increased to 28% with main reaction products  
 740 being methoxycyclohexanol, phenol, methoxycyclohexanone, cyclohexanol and  
 741 cyclohexanone with 9.8%, 7.8%, 4.6%, 2.7% and 1.2% yields, respectively. These results  
 742 suggest that methoxycyclohexanol and phenol are primary products obtained from GUA  
 743 transformation, as represented in Scheme 1. According to these results, guaiacol is expected  
 744 to adsorb in different configurations on the catalyst surface: (i) through the aromatic ring on  
 745 ZrO<sub>2</sub> sites, on flat  $\pi$ -adsorption configuration allowing the hydrogenation (HYD way) on  
 746 the close metallic Ni sites, and thus leading to the formation of methoxycyclohexanol [40,

747 106]; (ii) through the -OH/-OCH<sub>3</sub> groups on ZrO<sub>2</sub> sites, on a flat O-configuration allowing  
 748 hydrogenolysis catalysed by Ni particles, allowing the demethoxylation (DMO way)  
 749 leading to the formation of phenol [40, 41, 106, 107]. Methoxycyclohexanone was  
 750 observed to form at low reaction time. It can be produced by hydrogenation of guaiacol [32,  
 751 106]. Its further hydrogenation can lead to methoxycyclohexanol, which can produce  
 752 cyclohexanone by demethoxylation.



753

754 **Scheme 1.** Reaction pathway for the hydrodeoxygenation of guaiacol to cyclohexane on  
 755 silica supported Ni-ZrO<sub>2</sub> catalysts. HYD: hydrogenation, DMO: demethoxylation, DH:  
 756 dehydration.

757

758 The presence of phenol in a first stage of the reaction confirmed that the reaction pathway  
 759 included the demethoxylation of GUA to produce phenol, a step followed by the  
 760 hydrogenation to produce cyclohexanol via cyclohexanone intermediate [106]. The  
 761 presence of methoxycyclohexanol in the first stage of the reaction and the formation of  
 762 cyclohexanol prior to cyclohexane confirmed that the reaction pathway also included the  
 763 hydrogenation of GUA to produce methoxycyclohexanol, via methoxycyclohexanone  
 764 intermediate, a step followed by demethoxylation/hydrogenation to produce cyclohexanol,  
 765 via cyclohexanone intermediate. This means that at the beginning of the reaction, carbonyl  
 766 products can form but do not remain for a long time in the reaction mixture due to high  
 767 activity of the catalyst active phases. Finally, cyclohexanol produces cyclohexane via  
 768 dehydration to cyclohexene intermediate, which is likely rapidly hydrogenated as it is not  
 769 detected in the reaction medium.

## 770 **4. Conclusions**

771 Ordered mesoporous SBA-15 and KIT-6 silica materials were used as supports for  
772 confining Ni-ZrO<sub>2</sub> active phases. Incipient wetness impregnation (IWI) and two solvents  
773 (TS) methods were used for active phase deposition. Ni supported over mesoporous ZrO<sub>2</sub>  
774 support was also prepared for comparison. The deposition way has a significant influence  
775 on catalytic properties of the solid. High conversion of guaiacol is obtained when using the  
776 TS approach, with high yield obtained toward cyclohexane (~70%) at high guaiacol  
777 conversion degree (~90%). The better performances obtained using the TS approach are  
778 ascribed to a better distribution of active zirconia and nickel phases inside the mesopores,  
779 and a closer proximity between the Ni and ZrO<sub>2</sub> phases after activation. An additional  
780 benefit on the activity is obtained using support with 3-dimensional porosity (KIT-6)  
781 instead of 2-dimensional porosity (SBA-15). Finally, excellent stability is reported for silica  
782 supported confined Ni-ZrO<sub>2</sub> catalyst with no significant decrease in conversion and yield  
783 toward cyclohexane after 5 catalytic cycles. These results are evidences of the efficiency of  
784 the confining strategy to produce stable catalyst for HDO reactions. Evolution of  
785 conversion and product yields with reaction time over KIT-6 silica supported Ni-ZrO<sub>2</sub>  
786 particles showed that the hydrogenation and deoxygenation reactions proceeded through the  
787 formation of several intermediates, methoxycyclohexanol and phenol being the first  
788 detected, which were rapidly converted into cyclohexane. Using Ni supported over  
789 mesoporous zirconia led to significantly different catalytic properties. While the guaiacol  
790 conversion remained at a high level, reaction yield was oriented toward the production of  
791 cyclohexanol (~40%). For instance, it is demonstrated that finely dispersed ZrO<sub>2</sub>, in  
792 combination with confined Ni NPs, is far more efficient to promote deoxygenation  
793 reactions than Ni supported over bulk ZrO<sub>2</sub>.

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