**One-pot synthesis of cyclohexylphenol via isopropyl alcohol-assisted phenol conversion using the tandem system Raney Nickel plus hierarchical Beta zeolite**

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**Abstract**

Cyclohexylphenols are valuable intermediate chemicals applied in the manufacture of dyes, resins, and pharmaceutical drugs. However, they are synthesized using raw chemicals derived from fossil fuels rather than sustainable sources (e.g., lignin-derived phenol). In this article, we report a one-pot synthesis of cyclohexylphenols via phenol-assisted conversion with isopropyl alcohol over the tandem catalytic system formed by Raney Nickel plus hierarchical Beta zeolite. Over this tandem catalytic system, cyclohexylphenols were synthesized with remarkable selectivity (~ 70%) at high conversion rates (64%) after 1 h of reaction at 150º C. In contrast, higher temperatures (175 ºC) were required to obtain alkylphenols over Al-SBA-15 catalyst, which is highly accessible thanks to its uniform mesoporous structure, albeit with weaker Lewis acid sites. Additionally, selectivity to cyclohexylphenols over Al-SBA-15 was far lower (19%) than over hierarchical Beta zeolite, and cresols were instead the most abundant alkylphenol (26%). Therefore, the combination of suitable accessibility and Brønsted acidity of hierarchical Beta with the hydrogenating ability of Raney Ni through catalytic hydrogen transfer from isopropyl alcohol drive the selectivity of this tandem system towards the production of cyclohexylphenols.

**Keywords:** Raney Ni; isopropyl alcohol; phenol; cyclohexylphenols; hierarchical Beta; Al-SBA-15.

1. **Introduction**

The valorization of lignocellulosic biomass is a key goal worldwide for the production of both biofuels and raw chemicals, following the biorefinery approach1-4. Fossil fuels should be gradually replaced by bio-based chemicals to comply with the current demand for a sustainable economy. At present, the EU produces approximately 4.7 Mt/y of bio-based chemicals, which accounts for only 3% of the total market5. Consequently, new processes must be urgently developed to replace the fossil fuels by biomass-derived feedstocks in the production of chemicals.

Lignocellulosic biomass consists of three main constituents: cellulose, hemicellulose and lignin, whose relative share depends on the biomass6. For example, lignin ranges from 25 to 31 wt % in softwoods, from 16 to 24 wt % in hardwoods and from 16 to 21 wt % in herbaceous crops7. This polymer contains several aromatic units (e.g. synopyl alcohol (S), coniferyl alcohol (G) and p-coumaryl alcohol (H)) that may be harnessed as a source of valuable chemicals, such as phenol, alkylphenols or aromatic hydrocarbons7. Lignin depolymerization may be achieved using different treatments, including oxidative depolymerization, reductive depolymerization and thermal processes8,9. Among them, fast pyrolysis stands out as a rather promising approach for its simplicity (heating at 400 – 700 ºC under inert atmosphere) and high yields of bio-oils with a considerable content of phenolics compounds,e.g., phenol, guaiacols, catechols and alkylphenols10-12.

Alkylphenols are a family of compounds with several applications, e.g., cresols as antiseptic13, and butylphenols as antioxidants14, among others. In particular, cyclohexylphenols are highly valuable chemicals because they are employed in the manufacture various dyes, pharmaceutical drugs, resins and biocides15. But cyclohexylphenols are not found in significant concentrations in bio-oils produced by thermal/catalytic pyrolysis of lignin. Therefore, specific routes must be developed to produce them in large amounts from the initial phenolics16-18.

Cyclohexylphenols are traditionally obtained through two routes: a) phenol alkylation with either cyclohexene19-21 or cyclohexanol22, and b) phenol hydroalkylation23-26. In the first pathway, different catalysts, such as heteropolyacids (H3PW12O40) supported over mesoporous silica19,20 and zeolites (especially HY and H-Beta)21,22, have shown promising results, in terms of both conversion and selectivity. However, this route requires either cyclohexene or cyclohexanol alongside phenol in the initial reaction mixture. By contrast, the second pathway (phenol hydroalkylation) requires only phenol since cyclohexanol/cyclohexene are formed in the reaction medium from the starting reagent and, hence, can be considered more sustainable and efficient. In this regard, both Co2P/Beta24 and Ni/SiO2-Al2O326 catalysts catalyzed the synthesis of cyclohexylphenols with high selectivity in phenol hydroalkylation, albeit requiring high hydrogen pressures (40 – 100 bars) and temperatures (above 200ºC). For this reason, new routes should be explored for a one-pot synthesis of cyclohexylphenols under milder operation conditions.

In this context, several catalytic systems (Pd/Ce-Na27, Ni-Cu/Al2O328, Raney Ni29) have been reported for the conversion of aromatics and phenolics by transfer hydrogenation from alcohols. Among them, Raney Ni was particularly effective under mild conditions29-34. Moreover, transfer hydrogenation from alcohols over Raney Ni may lead to significant differences in selectivity in comparison with using pure hydrogen, as evidenced in the hydrogenation of dihydro-p-coumaryl alcohol (a building block of lignin)35. The combination of Raney Ni with zeolites has been used as a tandem catalytic system for transfer hydrogenation from isopropyl alcohol in phenol conversion into benzene36. The reaction mechanism proceeds through three stages involving the cooperative action between the metal sites of Raney Nickel (ring saturation and dehydrogenation) and the acid sites of Beta zeolite (dehydration). On the other hand, these results over the catalytic tandem system differ from those reported for supported bifunctional catalysts such as Ru/Al2O3-acidic that led mostly to cyclohexanol (90% yield) and cyclohexane (5% yield) in the catalytic hydrogen transfer of phenol with isopropyl alcohol using higher temperatures in comparison with the current one (225 ºC vs. 150 – 175ºC)37. In this regard, bifunctional catalysts (unlike the tandem system) require an adequate arrangement at the nanoscale of the metal and acid functions over the supported catalyst to maximize their performance in terms of activity and selectivity. Consequently, it is necessary not only to control the amount of deposited metal but to keep a suitable distance between both functions as well to attain the best catalytic results. This fact has been recently proved in the hydroconversion of n-alkanes towards branched hydrocarbons over Pt/HZSM-22/Al2O3 catalysts38.

In a previous study, we reported that the tandem catalytic system Raney Ni plus nanocrystalline or hierarchical ZSM-539 unveiled alkylation reactions in the phenol conversion alongside the expected reactions (ring saturation, dehydrogenation and dehydration). This alkylation shifted the selectivity towards bulky alkylphenolic products, cresols and cyclohexylphenols being the main ones obtained (36% and 17% selectivity respectively over Raney Nickel plus hierarchical ZSM-5 at 175ºC)39. Yet, despite such promising results, cyclohexylphenols were only produced with a modest selectivity (< 20%) over both hierarchical and nanocrystalline ZSM-5, which is distinctly lower than the one reported in this work over Raney Ni plus hierarchical Beta zeolite (~ 70%).

In the present study, we report a protocol for the one-pot synthesis of cyclohexylphenols from phenol with isopropyl alcohol with an enhanced selectivity (~ 70%) using the tandem catalytic system Raney Ni plus hierarchical Beta zeolite. Our system outperforms a similar tandem system consisting of Raney Ni plus Al-SBA-15. Both hierarchical Beta and Al-SBA-15 provide high accessibility to catalytic sites through their mesopores but differ considerably in acidity, which is a key factor in determining the formation of cyclohexylphenols, as disclosed below. Finally, this new route enables to obtain cyclohexylphenols with a high selectivity following a one-pot procedure instead a conventional two-stages strategy. Additionally, it takes place under milder reaction conditions in terms of temperature and pressure than conventional hydroalkylation pathways, thereby constituting itself a greener synthesis protocol to cyclohexylphenols. On the other hand, our results outperform those recently published in one-pot hydroalkylation work using Co2P/Beta that achieved lower selectivities towards cyclohexylphenols (56%)24.

1. **Experimental procedure**
   1. *Synthesis of the acidic catalysts*

Two different acid catalysts were used in this study: a hierarchical Beta zeolite (h-Beta) and a mesostructured Al-SBA-15 material. Both were synthesized with a silicon to aluminum molar ratio of 30 in the reaction mixture. The h-Beta material was prepared according to a protozeolitics units silanization method published elsewhere40. The following reagents were used: aluminum (aluminum flakes, Aldrich, 99.9 %), silica (fumed silica, Degussa), tetraethylammonium hydroxide (TEAOH, Alfa, 35% aqueous solution) and distilled water.

The Al-SBA-15 catalyst was prepared according to a method published in literature41 using aluminium isopropoxide (AIP, sigma-Aldrich, 99.9%), tetraethyl ortosilicate (TEOS, Sigma-Aldrich, 99%), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) Pluronic© P-123 ((EO)20-(PO)70-(EO)20, Aldrich), hydrochloric acid (Scharlab, 37%) and distilled water.

For comparison, two commercial Beta zeolites from Zeolyst International were used as references and named com-Beta-1 (Si/Al = 12.5) and com-Beta-2 (Si/Al = 19), respectively.

* 1. *Activation of Raney Nickel ®*

The reaction system requires an acidic function, which is provided by the h-Beta or Al-SBA-15 materials, as well as a hydrogenation/ dehydrogenation function. For the latter, a Raney Ni ® 2800 catalyst (Aldrich, Al content = 6-9%) was used. Raney Ni is a pyrophoric material provided as an aqueous dispersion. To remove water, the dispersion was rinsed with acetone three times and then with n-dodecane three more times and stored in n-dodecane until use. This was the most suitable method for achieving highly reproducible catalytic tests38.

* 1. *Catalyst characterization*

Raney Ni was not characterized due to its pyrophoric nature; however, the acidic catalysts were analyzed using different techniques. The crystalline structure of h-Beta was assessed by X-ray diffraction within the 5 – 70° range on a Philips X’Pert MPD diffractometer using Cu-Kα radiation. Low angle XRD, from 0.5° to 5°, was used to devise the mesostructure of Al-SBA-15. The Si/Al ratios were calculated by inductively-coupled plasma optical emission spectroscopy (ICP-OES) on a VARIAN Vista-PRO CCD Simultaneous spectrometer. The tetrahedral/octahedral aluminum ratios were determined by 27Al magic-angle spinning nuclear magnetic resonance (MAS NMR) on a Varian Infinity Plus 400 instrument at 104.16 MHz with spinning rates of 12 kHz.

The acid properties were assessed by FTIR spectra after pyridine adsorption to distinguish Lewis from Brønsted acid sites. These analyses were performed on a Nicolet iS 50 spectrophotometer with a spectral resolution of 4 cm-1 using 64 scans. The samples were pelletized to a self-supported sample disk of 10 mg/cm3, which was outgassed under vacuum at 450 ºC for 4 h. The disks were then saturated with pyridine, outgassed under vacuum at room temperature and, subsequently, subjected to several temperatures from 150 ºC to 450 ºC. The acid sites were determined using the following bands (vibration mode of pyridine) and absorption coefficients: pyridinium PyH+ band at 1545 cm−1 (ε = 1.67 cm·mol-1) and pyridine PyL band at 1455 cm−1 (ε = 2.2 cm·mol-1)42.

Lastly, the textural properties of the hierarchical Beta zeolite were characterized by Ar physisorption at -186.15 ºC on a Quantachrome Autosorb 1 apparatus, whereas those of Al-SBA-15 were determined by N2 physisorption at -196.15 º C on a Micromeritics Tristar 3000 device. Before the measurements, the Al-SBA-15 sample was degasified at 200 ºC for 8 h and the hierarchical Beta at 300 ºC for 3 h, respectively. The BET equation was applied to the 0.05 – 0.17 range of relative pressures to calculate the specific surface areas43. The total pore volumes were assessed at a relative pressure of 0.99. The pore size distributions were derived from the adsorption branch of the isotherms by applying the non-local density functional theory (NL-DFT)44 for h-Beta and the Barret-Joyner-Halenda (BJH) method for the Al-SBA-15 sample45. The external/mesopore surface area of Al-SBA-15 was determined using the t-plot method with the De Boer and Lippens equation46 to calculate the thickness (t) of the adsorbed monolayer within the 0.3 < p/p0< 0.5 range. The micropore surface area of Al-SBA-15 was calculated by subtracting the BET surface area from the external/mesopore surface area.

* 1. *Catalytic tests*

The phenol/isopropyl alcohol conversion tests were performed in 20 mL glass reactors stirred by a magnetic bean and heated by a silicone bath. Reactants and catalysts were carefully added to the reactor in the following order: 500 mg of Raney Ni; the corresponding amount of h-Beta or Al-SBA-15 to achieve a Ni/Al molar ratio of 80; 2 mmol of phenol (Aldrich, > 99%); 3.0 mmol of isopropyl alcohol (Aldrich, 99.5%) and 7 mL of n-dodecane (Aldrich, ≥ 99%). Inert atmosphere was ensured by flowing nitrogen through the reactor before placing it in the bath. Reaction tests were performed at three different temperatures, namely 125 ºC, 150 ºC and 175 ºC, for 5 to 240 minutes. Reference reactions were also performed at 150 ºC for 4 h with the same amount of acid catalyst but without Raney Ni.

Once the reaction was completed, the reactor was cooled down to room temperature. Then, 3 mL of ethyl acetate (Sigma-Aldrich, > 99.7%) was added, and the mixture was vigorously stirred for several minutes to a clear solution. Lastly, the liquid phase was separated from the catalysts by filtration.

The reaction mixture made up of phenol, isopropyl alcohol and n-dodecane was not homogeneous. Although phenol can be dissolved in isopropyl alcohol, since the alcohol was consumed along the reaction, most of the heavier reaction products solidified in the walls of the reactor during the cooling down, after the reaction was complete. However, during the reaction itself, the high temperature and fast stirring ensured that all the compounds were in the liquid phase forming a mixture as homogenous as possible. In light of these facts and for the sake of reproducibility, multiples of every reaction were conducted to make sure the results were correct.

GC-MS analyses were performed on a BRUKER SCION SQ 436-GC chromatograph equipped with an Rxi®-5Sil MS column to identify and quantify compounds heavier than phenol in the liquid phase. Before the analyses, the samples were further diluted in n-dodecane. Subsequently, the amount of compounds lighter than phenol was determined in a second GC analysis on a BRUKER SCION 456-GC equipped with an HP-INNOWax column and a FID detector. As an internal standard, 200 mg of a solution containing 50 mg of 1,2,3,4-tetrahydronaphthalene (Aldrich, 99%) and 7.5 g of n-dodecane was added to 400 mg of each sample.

From these analyses, the conversion of phenol (Xphenol), the selectivity to product j (Sj) and the yield of product j (Yj) were calculated as follows:

wherein minitial and mfinal stand for the mass of phenol initially loaded into the reactor and remaining in the liquid phase after the reaction, respectively, and mj accounts for the mass of every ring-containing liquid compound after the reaction. All the experiments were performed with an average carbon balance around 90 %. The detailed calculations of the mass balance have been included in the Supporting Information.

1. **Results and discussion**
   1. *Characterization of the catalysts*

The sample of the catalyst Raney Nickel® 2800 was purchased from Sigma-Aldrich and consists of a pyrophoric aqueous suspension that required working under an inert atmosphere. Therefore, this sample was not characterized, and the particle size (2-60 μm), surface area (80-100 m2/g) and chemical composition (Ni ≥ 89%, Al ≤ 6-9%) were provided by the manufacturer.

Figure 1a shows the XRD pattern of calcined zeolite h-Beta, displaying two main reflections centered at 2θ = 8º and 22º and other minor reflections, associated with two constituting polymorphs (A, B) of zeolite Beta47,48. Figure 1 b illustrates the low-angle XRD pattern of calcined Al-SBA-15. The most intense reflection at 2θ = 0.87º corresponds to the (100) plane and the less intense peaks at 1.53º and 1.77º to the (110) and (200) planes, respectively. Their presence indicates an ordered hexagonal porous structure49. However, these two latter reflections are less evident in this sample than in a pure silica SBA-15 sample because the introduction of Al into the SBA-15 structure resulted in a lower ordering of the mesoscopic arrangement41.



**Figure 1.** XRD patterns of calcined a) h-Beta and b) Al-SBA-15 samples

Figure 2a shows the Ar adsorption/desorption isotherms at -186.15 ºC of hierarchical Beta zeolite, which may be regarded as a combination of type I and type IV isotherms according to the IUPAC classification50. Figure 2b shows the pore sizes distribution obtained from the NL-DFT model applied to the adsorption branch. Ar adsorption at low relative pressures is due to the filling of the zeolitic micropores with sizes of approximately 6 - 7 Å. Additionally, Ar is also adsorbed in considerable amounts at intermediate relative pressures (P/P0 = 0.1 - 0.8), corresponding to mesopores present in this hierarchical zeolite samples, with sizes within the 20 - 80 Å interval51. The textural properties of the h-Beta sample are summarised in Table 1. The BET area is 606 m2 g-1, wherein 250 m2 g-1 is associated with the external/mesopore surface area. These results highlight the high accessibility of this material, showing a clearly bimodal pore size distribution.

**Table 1.** Physicochemical and textural properties of the acidic catalysts

|  |  |  |
| --- | --- | --- |
|  | **h-Beta** | **Al-SBA-15** |
| **Si/Al** | 24.4 | 38.0 |
| **BET surface area (m2 g-1)** | 606 | 839 |
| **Micropores surface area (m2 g-1)** | 356 | 73 |
| **External+mesopores surface area (m2 g-1)** | 250 | 766 |
| **Total pores volume (cm3 g-1)** | 0.42 | 1.40 |
| **Micropore volume (cm3 g-1)** | 0.21 | 0.04 |
| **External + mesopore volume (cm3 g-1)** | 0.21 | 1.36 |
| **Tetrahedral aluminum (%)** | 83 | 74 |
| **Octahedral aluminum (%)** | 17 | 26 |

The textural properties of Al-SBA-15 were derived from the N2 adsorption/desorption measurements at -196.15 ºC (Figure 2c) exhibiting a type IV isotherm, characteristic of mesoporous solids with an H1 hysteresis loop indicating uniform mesopores50. Condensation inside mesopores occurs around P/P0 = 0.75, thus suggesting large mesopores. The pores size distribution was assessed using the BJH method, giving rise to a narrow peak centred at 80 Å (Figure 2d). This material presented a specific surface area of 839 m2/g and a high total pores volume of 1.4 cm3 g-1, far higher than that of the hierarchical Beta zeolite (0.42 cm3 g-1), also showing some microporosity (0.04 cm3 g-1), as determined using the t-plot method.

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**Figure 2.** Adsorption-desorption isotherms of the acidic catalysts. a) Ar isotherm of h-Beta, b) NL-DFT pores size distribution of h-Beta, c) N2 isotherm of Al-SBA-15, d) BJH pore size distribution of Al-SBA-15

Table 1 outlines the Si/Al molar ratios of both samples measured by ICP-OES. The Si/Al ratio of h-Beta was 24.4, whereas that of Al-SBA-15 was 38. Despite adding a Si/Al atomic ratio of 30 in the synthesis gel, the Al content of the Al-SBA-15 sample was lower given the difficulty of incorporating Al into Al-SBA-15 pore walls. 27Al MAS-NMR was used to determine the tetrahedral and octahedral coordination of Al species in the framework of the catalysts52, cf. Table 1. The tetrahedral aluminium (chemical shift δ ~ 52 ppm) accounted for 83% in h-Beta and 74% in Al-SBA-15, with the remaining percentages corresponding to aluminium atoms with octahedral coordination (chemical shift δ ~ 0 ppm). This higher amount of octahedral Al found in Al-SBA-15 can be ascribed to the amorphous pore walls in the ordered mesoporous material.

Figure 3 illustrates the concentrations of Brønsted and Lewis acid sites for both catalysts, determined from FTIR pyridine adsorption spectra recorded at different evacuation temperatures. Hierarchical Beta contains more (0.37 vs. 0.18 mmol g-1 at 150 ºC) and stronger (0.19 vs. 0.07 mmol g-1 at 450 ºC) acid sites than Al-SBA-15. The concentration of acid sites over both catalysts at 150 ºC is lower than that expected considering their respective Si/Al atomic ratio, especially in Al-SBA-15, indicating the presence of octahedral aluminium in Al-SBA-15. The Lewis acid sites were the most abundant sites over both materials, regardless of temperature. The presence of additional porosity in zeolites has been reported to increase the share of Lewis acid sites53,54. Nevertheless, the hierarchical Beta zeolite has a higher concentration of Brønsted acid sites than Al-SBA-15. Thus, 37% of the acid site concentration of the zeolite and only 11% on the mesostructured Al-SBA-15 correspond to Brønsted centres at 150 ºC.



**Figure 3.** Concentration of Lewis and Brønsted acid sites in h-Beta and Al-SBA-15 catalysts measured at different pyridine desorption temperatures

* 1. *Catalytic tests*

1. *Reference tests in the absence of Raney Ni*

Initially, reference experiments of phenol conversion with isopropyl alcohol were performed using the acid catalyst (h-Beta or Al-SBA-15) in the absence of Raney Ni. These experiments aimed at adequately identifying the products formed via the acid catalyzed reactions to better compare them with those resulting from the tandem system. Accordingly, Figure 4 illustrates the conversion and product distribution of the reaction of phenol with isopropyl alcohol at 150 ºC for 4 h with only h-Beta or Al-SBA-15. Phenol conversion over h-Beta was 63%, but selectivity to diisopropyphenols was high (94%). In contrast, both phenol conversion (56%) and selectivity to diisopropyphenols (56%) over Al-SBA-15 were lower than those over hierarchical Beta. Additionally, over Al-SBA-15, a considerable amount of isopropyl phenyl ether was also detected (29%), most likely due to its weaker acidity, with a low share of Brønsted acid sites. No cyclohexylphenols were detected in both cases since the absence of Raney Ni precludes the extension of transfer hydrogen reactions.



**Figure 4.** Conversion and product selectivities in the reference reaction of phenol over h-Beta or Al-SBA-15 without Raney Ni (T = 150 ºC; t = 4 h)

1. *Influence of the reaction temperature over the tandem catalytic system*

The effect of the reaction temperature on the conversion of phenol with isopropyl alcohol over the tandem system Raney Ni plus a highly accessible acid catalyst (hierarchical Beta or Al-SBA-15) was investigated at three values (125, 150 and 175 ºC) in catalytic tests lasting 4 h. The atomic Ni/Al ratio was fixed at 80 since in previous experiments varying this ratio within the 40 – 360 range with the reference commercial Beta zeolite (com-Beta-1) the highest selectivity to benzene (64%) with a high phenol conversion (70%) was achieved (T = 150 ºC; t = 240 min). Figure S1 (see Supporting Information) illustrates these results wherein it can be appreciated that at lower Ni/Al atomic ratios than 80, the main products were phenolics compounds while at higher Ni/Al atomic ratios, the selectivity led mostly towards cyclohexanol and cyclohexanone. In this regard, an excessive amount of Raney Nickel virtually precludes the action of the acid zeolite, likely by its very low amount, taking place only catalytic hydrogen transfer reactions. Consequently, the tandem system works properly for a Ni/Al atomic ratio of 80, which is in agreement with earlier literature36.

Additionally, isopropyl alcohol was chosen because its high hydrogen transfer ability in contrast with other alcohols like ethanol that showed very low activity for hydrogen transfer. Figure 5 shows significant differences between the acid catalysts. At 125 ºC, conversion was higher over hierarchical Beta (52%) than over Al-SBA-15 (38%). However, when the reaction temperature increased up to 175 ºC, the catalysts provided similar conversions (58 and 62%, respectively). The maximum phenol conversion (68%) over hierarchical Beta at 150 ºC can be related to the decreased isopropyl alcohol availability at higher temperatures since this reagent undergoes a competitive reaction of dehydration to propene. In contrast, over Al-SBA-15, conversion increased steadily with the temperature because Al-SBA-15 has weaker and mostly Lewis acid sites, which are less affected by the competitive isopropyl alcohol dehydration.

The product distribution differed considerably in the absence (as discussed in the previous section) or presence of Raney Ni. Product diversity was higher with Al-SBA-15 in the tandem system and strongly varied with the temperature. Over this catalyst, the main products at the three tested temperatures were cyclohexene (39%, 125 ºC), benzene (40%, 150 ºC) and phenolics (60%, 175 ºC), respectively. In contrast, over h-Beta zeolite, phenolics were the main products, regardless of temperature, with selectivities surpassing 90%. In addition, benzene was detected with selectivities peaking below 6%.

Under the phenolics family, all phenol-related compounds were encompassed, including cresols, diisopropylphenols, cyclohexylphenols, butylphenols, and phenylisopropyl ether, among others (Figure 6). Over hierarchical Beta with Raney Ni, 60% selectivity to cyclohexylphenols was achieved at 125 ºC, subsequently decreasing with the increase in temperature. In parallel, the selectivity to diisopropylphenols increased with the temperature, reaching 57% at 175 ºC, and some cresols (14% selectivity) were obtained at 175 ºC. In contrast, over the tandem system with Al-SBA-15, high selectivity to phenolics, mostly consisting of cresols (26% selectivity) and cyclohexylphenols (19% selectivity), was reached only at 175 ºC. By comparison with the products in section 3.2.a), both cyclohexylphenols and cresols resulted from the cooperative action of the tandem mechanism because their preparation was not possible with only acid catalysis in the absence of Raney Ni.

The formation of both cyclohexene and benzene can be explained by a mechanism previously proposed in literature36 considering that the metal and acid sites act cooperatively through three sequential stages: a) phenol hydrogenation into cyclohexanol over Raney Ni by hydrogen transfer from isopropyl alcohol, b) cyclohexanol dehydration over the zeolite Brønsted acid sites originating cyclohexene and lastly, c) cyclohexene dehydrogenation over Raney Nickel giving rise to benzene. In this mechanism, the Raney Ni metal sites are involved the first and third proposed steps (a and c), whereas the acid sites promote the second one (step b).



**Figure 5.** Effect of temperature on phenol conversion and product selectivity over a) Raney Ni + h-Beta and b) Raney Ni + Al-SBA-15 (t = 4 h)



**Figure 6.** Effect of temperature on phenolic shares over a) Raney Ni + h-Beta and b) Raney Ni + Al-SBA-15 (t = 4 h)

Both Al-SBA-15 and h-Beta zeolite provide high accessibility to active sites thanks to their uniform mesoporous structure and bimodal micro/mesopore size distribution, respectively. In this regard, the formation of heavier compounds on the external/mesopore surface area of these zeolites is favored over conventional microporous zeolites with far higher steric constraints. This difference explains the formation of the bulky cyclohexylphenols in a reaction pathway that shares the first two steps with the aforementioned mechanism36, whereas the third step is the alkylation of phenol by the previously generated cyclohexene. Figure 7 shows the three steps of this modified mechanism leading to the formation of cyclohexylphenols.

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**Figure 7.** Cyclohexylphenol formation over the tandem system Raney Nickel plus h-Beta

The occurrence of step c) is supported by phenol alkylation experiments performed over zeolite Beta, as it was reported in the literature55,56. By *in situ* solid state NMR, it was demonstrated the formation of cyclohexyl carbenium ion over the zeolite Brønsted acid sites. In this regard, dehydration reactions of organic substrates containing alcohol moieties are known to occur over both Brønsted and Lewis acid sites, but the former are more relevant in kinetic terms57-60. Therefore, hierarchical Beta zeolite, which has more (0.14 vs. 0.025 mmol/g at 150 ºC) and stronger Brønsted acid sites than Al-SBA-15, favors the formation of cyclohexylphenols at relatively low temperatures. In contrast, over Al-SBA-15, cyclohexylphenols are produced only at higher temperatures (175 ºC) given its weaker acidity and a low content of Brønsted acid sites.

Over the tandem system with h-Beta, at higher temperatures, the Brønsted acid sites of the zeolite should be far more active than the Raney Ni metal sites, with the latter being virtually overturned. Thus, the direct alkylation of phenol with either isopropyl alcohol or propene, originated by prior dehydration of isopropyl alcohol over the h-Beta Brönsted acid sites, was extensively promoted, thereby favoring the formation of diisopropylphenols. As a result, the steps a) and c) of the tandem mechanism proposed elsewhere36 over the metal Raney Nickel sites almost disappeared. Under these experimental conditions, the tandem catalytic system ceased to work, and the product distribution approached that obtained without Raney Ni.

A previous study published in the literature using the tandem system Raney Ni plus an acid catalyst reported 79% selectivity to benzene (conversion of 98%) over Raney Ni plus conventional Beta zeolite under similar reaction conditions36. This marked difference from the results reported here over Raney Ni plus h-Beta zeolite can be ascribed to the hierarchical feature of this sample, which has 250 m2 g-1 of external/mesopore surface area. For this reason, this hierarchical Beta sample is much more active for alkylation reactions, bypassing step c) of the proposed mechanism36. Conversely, when using the tandem system Raney Ni plus hierarchical ZSM-539, the selectivity to cyclohexylphenols (17%) was close to that observed in the present study over Al-SBA-15 and considerably lower than that of h-Beta due to steric hindrance associated with the smaller micropores of ZSM-5. These smaller micropores make it difficult to accommodate the formation of cyclohexylphenols inside the pore structure of this zeolite. In this regard, cyclohexylphenol formation over the tandem system with h-ZSM-5 is primarily determined by the external/mesopore surface of the hierarchical zeolite, which shows a larger share of less active Lewis acid sites as well. Hence, the high selectivity to cyclohexylphenols achieved in this study over h-Beta may be ascribed not only to its acid properties but also to its enhanced accessibility because the formation of the bulky cyclohexylphenols is clearly favored over both mesopores and large micropores.

The formation of cresols and butylphenols is difficult to explain because they were unexpected products of the tandem mechanism. Nevertheless, we hypothesize that they may come from isopropyl alcohol/propene dimerization reactions over the catalyst acid sites, mostly leading to hexenes. Under this assumption, this step would be followed by its subsequent cracking into shorter alkyl moieties (C1, C2, C4), which would further alkylate phenol, ultimately resulting in the cresols and butylphenols. This chemistry resembles that proposed in the ethylene to propene conversion (ETP process) over Ni(II) single sites supported over Al-MCM-41 catalysts61.

1. *Influence of the reaction time over the tandem catalytic system with h-Beta*

Because the results showed that h-Beta zeolites are highly selective catalysts for the production of cyclohexylphenols, the reaction time was followed carefully. Figure 8.a) illustrates the evolution of the phenol conversion with isopropyl alcohol along time (from 5 to 240 min.) at 150 ºC over Raney Ni + h-Beta. The conversion quickly increased, reaching 27% after several minutes of reaction and subsequently increasing more slowly until reaching an almost steady value of 70% at 120 – 240 min. This plateau suggests the depletion of most of the isopropyl alcohol reagent by dehydration, and the evolution of the selectivity indicates that the main products were phenolics, whose share increased from 52% at 5 min. to more than 90% after 60 min. of reaction. In addition to phenolics, cyclohexanol was also produced with selectivity, but at very short reaction times. Thus, after 5 min. of reaction, selectivity to cyclohexanol reached 35%, subsequently decreasing over time until disappearing after 60 min. Conversely, benzene, which is the final product of phenol dehydroxylation over the tandem system in the mechanism proposed elsewhere36, is only produced with significant selectivity (6.3%) after 240 min. of reaction.



**Figure 8.** a) Effect of reaction time on phenol conversion and product selectivity and b) phenolic shares over Raney Ni + h-Beta

Figure 8.b) displays the time evolution of the different products of the phenolic family. At short reaction times, the main phenolic was isopropyl phenyl ether, whose selectivity was 43% at 5 min., subsequently decreasing until disappearing after 120 min. Accordingly, the formation of the O-alkylated product (isopropyl phenyl ether) was kinetically favored at the beginning of the reaction, but this product is subsequently transformed into C-alkylated species, which are more stable end products55. Similarly, because the etherification is an equilibrium reaction can be reversed on isopropyl alcohol consumption (see Figure 9)62, this reagent is released again from ether and can still act as a hydrogen source in the reaction medium. Thus, the share of cyclohexylphenols increased with the reaction time, with selectivity peakining at 69% (60 min). At longer reaction times (after 60 min.), the selectivity to phenolics shifted towards diisopropylphenols, so its share ramped up steadily, reaching approximately 35% at 240 min. In contrast, the corresponding selectivity to cyclohexylphenols at that time was merely 25%.



**Figure 9**. Etherification equilibrium between phenol and isopropyl alcohol

The decrease in selectivity to cyclohexylphenols was likely caused by two phenomena. First, heavier compounds might have been formed from cyclohexylphenols, as evidenced by GC-MS and in line with the production of heavier compounds in phenol hydroalkylation over Pd/C and Beta under hydrogen63. In this regard, bimolecular reactions such as disproportionation and transalkylation of cyclohexylphenols are favoured on the unconstrained external/mesopore surface of the hierarchical Beta zeolite. These reactions proceed at lower temperatures than dealkylation64 and result in both heavier products and phenol. Then, phenol may be further alkylated with remaining isopropyl alcohol or propene. Figure 10 shows the reaction scheme that may explain the increased selectivity to diisopropylphenols at longer reaction times at the expense of cyclohexylphenols. Additionally, the presence of Ni in ZSM-5 has been reported to enhance catalytic activity in toluene disproportionation65. Considering the above, Raney Ni, combined with hierarchical Beta in our tandem system, may also facilitate disproportionation reactions.

Diagrama, Esquemático

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**Figure 10**. Scheme of the disproportionation and alkylation reactions of cyclohexylphenols resulting in diisopropylphenols

Interestingly, over a tandem system formed by Raney Nickel plus a commercial Beta zeolite (com-Beta-2) with a similar mesopore size distribution but somewhat lower external/mesopore surface area (158 m2 g-1) than hierarchical Beta, the maximum selectivity towards cyclohexylphenol at 1 h of reaction was distinctly lower (51%) with a conversion of 68% under the same experimental conditions (Figure S2). This fact highlights the importance of a suitable mesoporosity for obtaining high yields of cyclohexylphenols.

Finally, the influence of the Si/Al atomic ratio of the hierarchical Beta zeolite harnessed in the tandem system with Raney Nickel was tackled. In this regard, a second hierarchical Beta sample, with a Si/Al = 15, was synthesized by the protozeolitic units silanization method as well40. Its main textural properties were as follows: a BET area of 711 m2 g-1 and micropore and mesopore surface area of 390 and 321 m2 g-1, respectively. Figure S3 illustrates the evolution of the phenolics shares along the time at 150ºC. It can be seen how the maximum selectivity towards cyclohexylphenols is reached at 60 min (58%) although it is a bit lower than that attained over Raney Nickel plus hierarchical Beta (Si/Al = 30). It is also noteworthy how at longer times (240 min.), the share of diisopropylphenols is higher than that over the tandem system with hierarchical Beta (Si/Al = 30). In this respect, it may be concluded that an excessive amount of acid sites is detrimental for optimizing the selectivity towards cyclohexylphenols as they are converted into heavier species.

1. **Conclusions**

Phenol conversion with isopropyl alcohol over h-Beta without Raney Ni mostly yields diisopropylphenols by direct alkylation over zeolitic Brønsted acid sites, whereas Al-SBA-15 produces a mixture of diisopropylphenols and isopropyl phenyl ether as well.

Combining Raney Ni with a zeolite in a tandem catalytic system completely changes the product distribution. In this respect, previous experiments with a commercial Beta zeolite (com-Beta-1) demonstrated that an Ni/Al atomic ratio of 80 was optimum for the tandem system to work properly, being this ratio chosen for all the experiments. Raney Nickel plus hierarchical Beta allow the one-pot synthesis of cyclohexylphenols with a high selectivity (~70%). In contrast, over Raney Nickel with Al-SBA-15, the selectivity to cyclohexylphenols barely reaches 19% and is surpassed by other products such as benzene, cyclohexene or cresols, depending on the reaction temperature. The preferential formation of cyclohexylphenols over Raney Ni plus hierarchical Beta results not only from the high accessibility of this zeolite, derived from its mesoporosity, but also to its appropriate content of Brønsted acid sites and large micropores. Additionally, this hierarchical zeolite surpasses in the tandem system with Raney Nickel the selectivities towards cyclohexylphenols obtained when using either a commercial Beta zeolite (com-Beta-2) with similar mesoporosity but lower external/mesopore surface area or another hierarchical Beta with superb accessibility although lower Si/Al atomic ratio.

The cyclohexylphenol formation is explained by a modified mechanism of the tandem system, involving three steps: a) phenol hydrogenation to cyclohexanol, b) cyclohexanol dehydration to cyclohexene and c) phenol alkylation to cyclohexylphenol with cyclohexene. Two of these steps are catalyzed by the Brønsted acid sites (b and c) and the other by the Raney Nickel metal sites (step a).

In summary, the high selectivity to cyclohexylphenols appreciated over the tandem system Raney Ni plus hierarchical Beta can be ascribed to the high accessibility of this zeolite resulting from its hierarchical pore structure and to the zeolite Beta micropores, with a high content of strong Brønsted acid sites. As a result, this catalytic tandem system enables the one-pot synthesis of cyclohexylphenols with high activity and selectivity. Additionally, the route reported in the present study takes advantage of catalytic hydrogen transfer from alcohols to yield cyclohexylphenol under milder reaction conditions than those previously reported for phenol hydroalkylation with molecular hydrogen.

1. **Author contributions**

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1. **Conflicts of interest**

There are no conflicts of interest to declare.

1. **Acknowledgements**

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**Supporting information**

**Calculation of mass balances and selectivities**

The mass balances were calculated according to a conventional definition, comparing the total mass detected after the reaction with the total mass of the reactants:

where is the total mass of reactants and products detected by GC-FID analyses after the reaction and is the total mass of starting reactants, which is weighed before the reaction.

The masses after reaction were calculated as accurately as possible from the GC-FID analyses. We used an internal standard for the analyses (1,2,3,4-tetrahydronaphthalene), so the area of the peaks could be converted into mass irrespectively of the amount of sample injected (manually) in that particular run. Besides, after injecting known amounts of each of the main compounds, we calculated response factors for those. For the internal standard and for any minority or unknown compound a response factor of 1 was applied.

Each mj value was calculated as follows:

where Aj is the chromatographic area of the corresponding peak and Fj is the response factor of the specific compound and R is the mass/area ratio of the internal standard in that specific analysis.

The compounds measured in the GC-FID analyses are shown in Table S.1.

**Table S.1.** Compounds measured for the calculation of mass by GC-FID analysis.

|  |  |
| --- | --- |
| Compound | Compound |
| Benzene | Methyl isobutyl ketone |
| Cyclohexane | Internal standard |
| Cyclohexene | Phenol |
| Acetone | Diisopropylphenols |
| 2-propanol | Cyclohexylphenols |

On the other hand, the GC-MS analyses pointed out that the observed broad peaks of diisopropylphenols and cyclohexylphenols (the only ones visible at higher retention times) in the GC-FID analyses were indeed a mixture of different phenolics that could not be properly separated and identified in the GC-FID analyses. Consequently, the corresponding selectivities towards phenolics was calculated based on the GC-MS distribution, assuming a response factor of 1.

Gráfico, Gráfico de barras, Gráfico en cascada

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**Figure S1.** Conversion of phenol and product distribution attained in the reactions with the tandem system Raney Ni plus com-Beta-1 varying the Ni/Al atomic ratio (T = 150 ºC; t = 240 min; molar ratio isopropyl alcohol / phenol = 1.5; catalyst: com-Beta-1 (Si/Al = 12.5; SBET = 625 m2 g-1).

Gráfico, Gráfico de barras

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**Figure S2.** Effect of the reaction time on the phenolics share over the tandem system Raney Nickel plus com-Beta-2 (T = 150º C; molar ratio isopropyl alcohol/phenol = 1.5; catalyst: com-Beta-2 (Si/Al = 19; SBET = 633 m2 g-1).

Gráfico, Gráfico de barras

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**Figure S3.** Effect of the reaction time on the phenolics share over the tandem system Raney Nickel plus hierarchical Beta (Si/Al = 15, SBET = 711 m2 g-1) (T = 150º C; molar ratio isopropyl alcohol/phenol = 1.5).