**Shifting pathways in the phenol/2-propanol conversion over the tandem Raney Ni + ZSM-5 catalytic system**

A. M. García-Minguillán1, L. Briones1, D. P. Serrano2, J. A. Botas1, and J. M. Escola1,\*

1Group of Chemical and Environmental Engineering, Rey Juan Carlos University, c/ Tulipán s/n, 28933, Móstoles, Madrid (Spain)

2IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, 28935, Móstoles, Madrid (Spain)

\* to whom correspondence should be addressed

e-mail: josemaria.escola.saez@urjc.es

Tel: +34 91 488 70 88

**Abstract**

This work investigates the effects of both the zeolite accessibility and the reaction temperature on conversion of phenol assisted by 2-propanol over the tandem system Raney Ni + ZSM-5 zeolite. Two different zeolite samples, containing similar Si/Al ratios, were used: nanocrystalline ZSM-5 (n-ZSM-5) and hierarchical ZSM-5 (h-ZSM-5), operating at temperatures of 125, 150 and 175°C. When working with the Raney Ni + n-ZSM-5 system at low and intermediate temperatures the main products were mostly benzene and cyclohexene formed by phenol deoxygenation. In contrast, when increasing the temperature up to 175°C, a shift in the reaction pathways was observed, leading towards a significant share of valuable alkylphenols (mostly cresols and cyclohexylphenols) in the product distribution, generated by the occurrence of alkylation reactions catalyzed by the zeolite acid sites. This effect was enhanced in the case of the h-ZSM-5 sample, due to its improved accessibility and larger mesopore/external surface area.

**Keywords:** Raney Ni; hierarchical ZSM-5; phenol; alkylphenols; cresols; 2-propanol

1. **Introduction**

Lignocellulosic biomass constitutes an abundant and renewable source of chemicals and biofuels. Thereby, depolymerization of its three main components (cellulose, hemicellulose and lignin) into lighter products is required1-3. A relatively easy way to carry out the lignocellulose transformation and valorization is by fast pyrolysis (thermal or catalytic), rendering high yields of bio-oil (the liquid fraction), which is a potential source of more than 300 chemicals4-6. However, these bio-oils need further catalytic upgrading to increase the share of valuable products.

A variety of catalytic routes, based on hydrogen transfer reactions, have been proposed to upgrade the bio-oil or even to promote the transformation of the raw biomass7,8. Thus, using Raney Nickel and 2-propanol as hydrogen transfer reagent woody biomass was converted into a non-pyrolytic lignin and carbohydrates9,10. Additionally, reduction of the phenolic compounds present in the bio-oil by hydrogen transfer with 2-propanol over Raney Nickel has led mostly to cyclic alcohols and less functionalized alkylphenols11. Interestingly, these hydrogen transfer reactions were carried out under low severity conditions in terms of both pressure (autogenous) and temperature (60 – 220 ºC). As demonstrated in the hydrogenation of dihydro-p-coumaryl alcohol, the use of 2-propanol over Raney Ni led to different results from those attained with molecular hydrogen. Thus, only ring saturation was observed with molecular hydrogen while with 2-propanol both ring hydrogenation and hydrodeoxygenation took place, denoting the interest of using 2-propanol as H-transfer agent12. However, some abatement of the Raney Nickel activity has been observed due to the presence of hemicellulose sugars13 and the occurrence of other alcohols in the medium14. Likewise, both formic and acetic acids have also been reported to have a detrimental influence upon Raney Nickel performance in hydrogen transfer reactions15.

On the other hand, Raney Nickel has been proved to be a rather specific catalyst in hydrogen transfer hydrogenation, showing quite different activity patterns for even positional isomers of methoxyphenols, depending on their respective adsorption mode over Raney Ni surface16. In addition, Raney Nickel has also been applied in hydrogen transfer reactions with 2-propanol for the valorization of alkyl levulinates to obtain valuable platform chemicals such as γ-hydroxypentanoates and γ-valerolactone17. Moreover, it has also been reported the transformation of glucose to sorbitol over Raney Ni by hydrogen transfer reactions in the presence of short chain alcohols18. Additionally, aromatic ketones have been hydrodeoxygenated to alkylaromatics by hydrogen transfer with 2-propanol over Raney Ni19.

Hydrogen transfer reactions with 2-propanol have also been investigated over tandem catalytic systems comprising both Raney Ni and an acid catalyst. The latter may catalyze both hydrolysis and dehydration reactions, leading to important changes in the product distribution. Thus, high yields of aromatic compounds have been obtained from both bio-oil and phenol using the tandem system Raney Ni + Beta zeolite in the presence of 2-propanol as hydrogen-donor20. Likewise, Jiang et al.21 have reported the depolymerization of cellulolytic enzyme lignin into monomeric phenols over Raney Ni + acidic zeolite catalysts in the presence of methanol/water solutions. Likewise, Huang et al.22 concluded that the combination of acidic zeolites with Raney Ni, using methanol for the in-situ hydrogen generation by aqueous phase reforming, increased the conversion of phenol to produce cyclohexanone and cyclohexanol. These works evidence the high potential and interest of coupling Raney Ni and zeolite catalysts for the conversion of biomass-derived compounds assisted by alcohols 23.

In the present work, and with the aim of obtaining high added-value compounds, the phenol/2-propanol conversion has been studied using the tandem reaction system Raney Ni + ZSM-5. This zeolite was also one of the materials investigated in the work of Wang and Rinaldi20, although the major focus of that work was put on zeolite Beta, whereas the properties of the ZSM-5 sample employed were little disclosed. In comparison with zeolite Beta, ZSM-5 it is well known to exhibit a stronger acidity with a higher proportion of Brönsted acid sites, although it may suffer of strong limitations for the processing of bulky compounds, as those present in bio-oil, due to its relatively small micropore size. To overcome these hindrances, in the present work ZSM-5 samples with enhanced accessibility have been employed, comprising nanocrystalline and hierarchical ZSM-5 zeolites. The results so obtained show that varying both the ZSM-5 zeolite features and the reaction temperature modifies sharply the attained selectivity pattern originating a shift in the reaction pathways. Thus, the product distribution may be driven either towards benzene / cyclohexane or alkylphenols instead. The latter are valuable products, with applications in the preparation of anesthetics, dyes, antiseptics, thermal stabilizers, aromas, flavors, disinfectants and drugs preservatives24-26.

1. **Experimental**
   1. *Catalyst preparation*

The catalytic tandem system here employed consists of Raney Ni + ZSM-5 zeolite, wherein the metal provides the hydrogenating/dehydrogenating functions and the zeolitic component the acidity. The Raney Ni® sample (Raney Ni 2800, Al content = 6-9%, Aldrich, aqueous dispersion) is a high-surface-area (80 – 100 m2/g) pyrophoric nickel-aluminum alloy. Prior to the reaction, three different procedures were tested for the conditioning of the metal catalyst: a) Raney Ni was poured into the reactor directly from the aqueous suspension, avoiding any water excess; b) water was removed from the Ni dispersion by rinsing a small amount with acetone three times and then with n-dodecane three more times; c) a larger amount of Raney Ni was washed as in b) and then stored in n-dodecane until being used (the maximum storage time was less than 72 h to avoid effects coming from a possible degradation of the Raney Ni system). After checking all of them, procedure c) was found as the most convenient in order to achieve a high reproducibility in the catalytic tests.

Two different zeolite samples were employed in this work. The first one is a commercial nanocrystalline ZSM-5 (n-ZSM-5) provided by Südchemie with a Si/Al molar ratio of 30. The other zeolite sample is a hierarchical ZSM-5 (h-ZSM-5) with Si/Al = 32, prepared by crystallization of silanized protozeolitic units according to a procedure published elsewhere27,28. Thereby, a gel with a Si/Al molar ratio of 30 was prepared, having the following composition: Al2O3 : 60 SiO2 : 11 TPAOH : 1500 H2O. The reagents employed were tetraethylortosilicate (TEOS, Aldrich, 98%) as silicon source, tetrapropylammonium hydroxide (TPAOH, Alfa, 40% v/v aqueous solution) as structure directing agent, aluminum isopropoxide (AIP, Aldrich) as aluminum source, and distilled water. The gel was precrystallized at 90°C for 20 h and, thereafter, it was subjected to silanization at 90°C for 6 h under reflux with phenylaminopropyltrimethoxysilane ((C6H5)NH(CH2)3Si(OCH3)3, Aldrich, > 97%). The resulting mixture was then crystallized at 170°C for 7 days. Finally, the solid product was washed with distilled water and recovered by centrifugation at 5000 rpm for 10 minutes (three times), dried overnight at 110°C and calcined in stagnant air at 550°C for 5 h.

* 1. *Catalyst characterization*

Due to the pyrophoric nature of Raney Ni, it was not subjected to any characterization, whereas the zeolitic catalysts were analyzed by several techniques. The crystalline structure of the samples was inferred from X-ray diffraction (XRD) patterns that were collected within the 5 – 70° range in a Philips X’Pert MPD diffractometer using Cu-Kα radiation with a step size of 0.1° and a counting time of 10 s. The Si/Al ratio was obtained by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) on a VARIAN Vista AX Axial CCD Simultaneous spectrometer. Thereby, the zeolite samples were dissolved by acid digestion in HF and H2SO4 prior to the analysis.

The acid properties of the zeolite samples were determined by temperature-programmed desorption of ammonia (NH3-TPD) in a Micromeritics AutoChem 2910 apparatus. The catalysts were first saturated with 10% NH3 in He at 180°C. Then, the physisorbed ammonia was removed by flowing helium for 30 minutes. The chemisorbed NH3 was finally released by increasing the temperature up to 550°C with a heating rate of 15°C/min and measured with a thermal conductivity detector.

The shares of tetrahedral and octahedral aluminum species were determined by the signals at 54 and 0 ppm, respectively, in the 27Al magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra obtained in a Varian Infinity Plus 400 instrument operating at 104.16 MHz with spinning rates of 12 kHz. Chemical shifts were referenced to Al(H2O)63+ as external standard. Images of the zeolites were taken by transmission electron microscopy (TEM) collected in a Philips TECNAI 20 microscope with a LaB6 filament under an accelerating voltage of 200 kV.

The textural properties of the zeolite catalysts were derived from the Ar adsorption-desorption isotherms at -186.15 ºC obtained in a Quantachrome Autosorb 1 instrument. BET surface areas were calculated using relative pressures between 0.05 and 0.17 as range of linearity. Total pore volumes were calculated at a relative pressure of 0.99. The cumulative pore volumes and pore size distributions, as well as the contribution of both micro- and mesoporosity, were determined by applying the non-local density functional theory (NLDFT) model to the Ar adsorption branch of the isotherm assuming cylindrical pore geometry.

* 1. *Phenol/2-propanol conversion tests*

The catalytic tests were performed in 20 mL glass reactors provided with a magnetic stirrer and heated by a silicone oil bath. Reactants (all from Aldrich) and catalysts were added in the following order: 500 mg of Raney Ni; 185 mg of zeolite; 2 mmol of phenol (purity > 99%); 3.0 mmol of 2-propanol (99.5%) and 7 mL of n-dodecane (≥ 99%). To ensure inert atmosphere, air was removed from the reactors by flowing nitrogen. Reactors were placed into the oil bath to reach the desired temperature. The reactions were carried out at different temperatures (125, 150 and 175°C) for 4 h. After this time, the reactors were removed from the bath and allowed to cool down to room temperature.

After separating the solid catalysts by filtration, the resulting liquid mixture was homogenized by adding 3 mL ethyl acetate (Sigma-Aldrich, > 99.7%). Liquid products were identified by gas chromatography – mass spectrometry (GC-MS) in a BRUKER SCION 436-GC coupled to a mass detector and quantified in a BRUKER 456-GC equipped with a FID detector. In order to accurately quantify all products, 50 mg of tetralin (Aldrich, 99%), used as internal standard, was dissolved in 7.5 g of n-dodecane and 200 mg of this solution was added to 400 mg of each sample prior to the analysis. For the major compounds, commercial samples were purchased and used to obtain calibration curves. In selected tests, samples of the gases were taken from the reactor with a syringe through the rubber septum before the addition of ethyl acetate, being analyzed in a Varian 3800 GC apparatus and identified using the Varian Star Detailed Hydrocarbon Analysis 5.0 software.

1. **Results and discussion**
   1. *Characterization of the zeolite samples*

Both ZSM-5 zeolite samples used in this work (n-ZSM-5 and h-ZSM-5, respectively) were fully characterized by different techniques: XRD, 27Al MAS NMR, NH3 TPD, Ar adsorption-desorption isotherms at -186.15 ºC and TEM.

Figure 1.a) depicts the XRD patterns of the zeolite samples wherein both materials exhibit the main diffraction peaks corresponding to the MFI zeolitic structure29-31. No broad shoulder around θ ~ 23- 25° is observed, bearing out the high crystallinity of these samples. The Ar adsorption-desorption isotherms, recorded at -186.15 ºC, of both samples are displayed in Figure 1.b). As zeolites are microporous materials, a great part of the adsorption occurs at low relative pressure. In addition, Ar uptake at intermediate pressure can be also observed, especially for the hierarchical ZSM-5 sample, denoting the significant contribution of external and/or mesopore surface area. The adsorption and desorption branches of the isotherms are rather close for both zeolites, so they show small hysteresis loops. For the sample n-ZSM-5, the hysteresis loop is present at very high relative pressure, which is indicative of being originated by interparticle voids. In the case of h-ZSM-5 sample, the hysteresis loop shape is relatively close to type H4 of the IUPAC classification, which is often found in aggregated crystals of zeolites and some mesoporous zeolites31. The enhanced accessibility exhibited by h-ZSM-5 is reflected in the values of its textural properties32,33. Thus, at shown in Table 1, higher BET surface area, total pore volume and external/mesopore surface area are observed for h-ZSM-5 compared to n-ZSM-5. Nevertheless, both materials present significant mesopore/external surface areas, with values of 128 and 273 m2/g for n-ZSM-5 and h-ZSM-5, respectively, which confirm their improved accessibility regarding to conventional ZSM-5 zeolite. Moreover, the h-ZSM-5 sample possesses mesopores with a mean diameter of 3.4 nm, in agreement with its hierarchical porosity. For this sample, the secondary porosity represents, in terms of surface area, around half of the overall one.

Figure 2 illustrates TEM images of both zeolites. The n-ZSM-5 sample is made up of irregular agglomerates of nanocrystals with a relatively broad size distribution (in the range 50 – 90 nm), confirming the nanocrystalline features of this material. In contrast, the h-ZSM-5 micrographs display globular shape particles with a size within 200 – 400 nm, which are actually formed by aggregation of smaller zeolitic nanounits with a size between 5 and 15 nm. The voids existing between the nanounits are the origin of the secondary porosity present in the hierarchical ZSM-5 sample.

As shown in Table 1, the Si/Al atomic ratio is very similar for n-ZSM-5 and h-ZSM-5 samples (30 and 32, respectively). In order to get insights about the state and coordination of the Al atoms, the 27Al MAS NMR spectra of the ZSM-5 zeolites were recorded (Figure 3). Both samples present a major peak with a chemical shift of δ ~ 54 ppm, corresponding to tetrahedral aluminum. In addition, octahedral Al species with a chemical shift of δ ~ 0 ppm are detected, although in low concentration34. Thus, a great share of the Al species present in both samples (> 90%) exhibit tetrahedral coordination, being incorporated into the ZSM-5 framework.

Table 1 summarizes the acid properties of the ZSM-5 samples determined by NH3 TPD, including the overall acidities and temperature maxima of ammonia desorption. Both h-ZSM-5 and n-ZSM-5 possess acid sites of high strength, since their maximum temperature of ammonia desorption is in the range 350 - 357°C. The total acidity of n-ZSM-5 is 0.35 mmol NH3/g, being somewhat above that of h-ZSM-5 (0.31 mmol NH3/g), which can be assigned to the lower Si/Al atomic ratio of the former.

* 1. *Phenol/2-propanol conversion tests*

The catalytic tandem system Raney Ni + ZSM-5 zeolite has been tested in the conversion of phenol assisted by 2-propanol. The reactions were carried out at three different temperatures 125, 150 and 175°C. The use of two different zeolite samples (n-ZSM-5 and h-ZSM-5) is aimed at checking the effect of the acid catalyst accessibility.

Figure 4.a) illustrates the phenol conversion and the products distribution obtained over the tandem system Raney Ni + n-ZSM-5 at the three studied temperatures while Figure 4.b) depicts the selectivity within the phenolics family, which includes the different alkylphenols and phenyl ethers being detected. The phenol conversion increases only slightly with the reaction temperature, from 38% at 125°C to 43% at 175°C. Taking into account the feed composition (2-propanol/phenol = 1.5) and considering that the required stoichiometric ratio 2-propanol/phenol is over 3, depending on the final product, these results evidences the high activity of the tandem system. Likewise, it should be borne in mind that, in addition to its role as H-transfer agent, 2-propanol can participate in the reaction medium in a variety of secondary reactions, such as dehydrogenation over Raney Ni and dehydration over the zeolitic acid sites, releasing propene and thus decreasing the 2-propanol availability in the liquid reaction medium. In this way, the presence of propene in the gaseous phase has been confirmed by GC analyses.

As illustrated in Figure 4.a), sharp changes in the product distribution take place with the rise in the reaction temperature. Thus, the major product at 125 and 150°C was cyclohexene, while at 175°C phenolics and benzene were the main components. This strong variation of product selectivity with the temperature suggests that phenol conversion may proceed through different reaction pathways.

At the lowest reaction temperature (125°C), cyclohexene is the major product, being obtained with a selectivity of 57%, followed by benzene (16% selectivity). Other hydrocarbon, detected in lower concentration, is cyclohexane. In addition, oxygenated compounds, such as cyclohexanone, cyclohexanol and phenolics different from phenol, are also identified in the reaction medium. This product distribution agrees well in general with that earlier reported20, although in that case cyclohexene was not identified among the reaction products. In order to check whether this difference could be related to the mode of conditioning the Raney Ni catalyst, a variety of pre-treatments for this catalytic system were checked (see experimental section). In all cases significant amounts of cyclohexene were detected in the product distribution, confirming that the appearance of this product was not dependent on the Raney Ni conditioning procedure. Moreover, the procedure finally selected, and then employed in all catalytic tests, provided the best reproducibility of the reaction results.

Taking into account previous literature works20,35, as well as the product selectivity pattern here obtained, the reaction scheme shown in Figure 5 is proposed to account for the pathway occurring at low temperature, which yields different hydrocarbons as main final products. Initially, in reaction 1, phenol is hydrogenated over Raney Ni towards cyclohexanone by hydrogen transfer. In reaction 2, cyclohexanone is further reduced over Raney Ni to give cyclohexanol. 2-propanol is assumed to be the major reduction agent, although the occurrence of some hydrogen-transfer from cyclohexene is not discarded in agreement with the conclusions of Wang and Rinaldi20. In reaction 3, cyclohexanol is dehydrated over the acid sites of the ZSM-5 zeolite, producing cyclohexene. Subsequently, cyclohexene may undergo both hydrogenation/dehydrogenation reactions catalyzed by the metal component of the tandem system. Thus, according to reaction 4, cyclohexene is dehydrogenated over Raney Ni yielding benzene. Finally, cyclohexene can be hydrogenated towards cyclohexane (reaction 5).

On increasing the reaction temperature, the overall selectivity towards the products included in the reaction pathway of Figure 5 dropped from 89% at 125°C to 50% at 175°C. Cyclohexanone was attained with a selectivity of roughly 7% at 125°C and it decreased to almost zero at 175°C. Likewise, the selectivity towards cyclohexanol remained very low (< 4%) at both 125 and 150°C and it was virtually null at 175°C, which is indicative of the fast kinetics of the alcohol dehydration reaction over the ZSM-5 zeolite acid sites. Likewise, the selectivity towards cyclohexene decreased steadily from 57% at 125°C to 12% at 175°C, showing that this compound is sharply consumed when increasing the reaction temperature. Cyclohexane, obtained through reaction 5 (Figure 5), showed also a low selectivity (about 3-6%) at the three studied temperatures. In contrast, the selectivity towards benzene increases distinctly from 16% (125°C) to 34% at 175°C, which is in agreement with this hydrocarbon being a final product in the reaction scheme of Figure 5.

Interestingly, a sharp increase in the overall selectivity towards phenolics, from 6% to 50%, is observed with the rise of the reaction temperature. Figure 4.b) illustrates the selectivity towards the main phenolics components at the three studied temperatures over the tandem system Raney Ni + n-ZSM-5 zeolite. These phenolics comprise alkylphenols (cresols, diisopropylphenols, cyclohexylphenols, butylphenols) and phenyl ethers (isopropylphenyl ethers), respectively. Alkylphenols have been also reported as the main products of the catalytic fast pyrolysis of biomass over KZSM-5 zeolite, although in vapor phase and at much higher temperature (500°C)36. These alkylation reactions are expected to occur mostly on the accessible acid sites placed at the external surface of the zeolite sample, since the so attained alkylphenols are rather bulky molecules in comparison with the ZSM-5 micropores. On the other hand, to explain the origin of cresols in this system poses some challenges since they are not likely being formed by direct alkylation of phenol, considering the absence of methanol in the reaction medium. Interestingly, a blank reaction was carried out at 150°C using just n-ZSM-5, without Raney Ni and no cresol was present in the products makeup. In addition, methane and ethane were detected in the gaseous phase, suggesting the occurrence of hydrogenolysis reactions in our medium37,38. The whole of these data suggests that the production of cresols (chiefly the meta- isomer) occurs by a combined action of both the acid sites of the zeolite and the Raney Nickel metal sites. Since isopropylphenols were not detected in our product makeup, it can be assumed that they are consumed in the formation of either cresols or diisopropylphenols by a competing second alkylation. In this way, it is noteworthy to point out that the molar ratio of (cresols)/(diisopropylphenols) is about 57 over the tandem system with n-ZSM-5 at 175 ºC, denoting the rather faster kinetics of cresols formation in comparison with the alkylation of isopropylphenols.

Cyclohexylphenols represent other alkylphenols of interest observed in the reaction medium, especially 2-cyclohexylphenol. The latter is a high-added value product since it is precursor of o-phenylphenol, which is commonly employed as dye, antiseptic and thermal stabilizer25. Cyclohexylphenols are formed by alkylation of phenol with cyclohexene. In this regard, the alkylation of phenol with cyclohexene over H-Beta zeolite has been recently reported yielding mostly 2 and 4 cyclohexylphenols at longer reaction times39, which agrees well with the results of the present work. This reaction requires a high catalyst accessibility to afford the formation of the bulky cyclohexylphenols, hence it is expected to occur over the acid sites placed on the external surface of the n-ZSM-5 nanocrystals.

Among the phenolics compounds, isopropylphenyl ethers were also detected, although in small amounts, with a selectivity of 4 – 6% at the lower temperatures (125, 150°C), while its presence at higher temperature (175°C) was virtually negligible. This finding denotes that the etherification reaction between phenol and 2-propanol proceeds in very low extent over the tandem system Raney Ni + n-ZSM-5.

Subsequently, the influence of the zeolite accessibility was ascertained using a hierarchical ZSM-5 zeolite (h-ZSM-5), which possesses a high share of mesopore/external surface area, in the tandem system along with Raney Ni. Figures 6.a) and b) illustrate the results so obtained in the transformation of the phenol/2-propanol mixture. The conversion increased slightly with temperature, reaching values around 43 - 45% at 150 – 175°C.

At 125°C, the main product was cyclohexene (44%), followed by benzene and phenolics with similar selectivities (17%). This fact denotes the positive effect of increasing the ZSM-5 accessibility on the cyclohexanol dehydration reaction. As a whole, at this temperature the overall selectivity towards benzene, cyclohexene, cyclohexane, cyclohexanol and cyclohexane, obtained through the pathway outlined in Figure 5, is somewhat lower (78%) than that corresponding to the use of the nanocrystalline ZSM-5 sample in the tandem system (89%). In contrast, at higher temperatures (150 and 175°C), the formation of phenolics is the preferred reaction route with selectivities of 70 and 83%, respectively. These values are far higher than those above obtained over the tandem system Raney Ni + n-ZSM-5. The benzene selectivity was around 17% over h-ZSM-5 at these two temperatures while the selectivity towards cyclohexanol, cyclohexene and cyclohexanone dropped with the temperature increase, being practically negligible at 175°C. Accordingly, the extent of the pathway outlined in Figure 5 is rather limited when using the hierarchical ZSM-5 at the two higher temperatures since, in this case, alkylation reactions are strongly favored. Therefore, in spite of the fact that both n-ZSM-5 and h-ZSM-5 possess the same MFI structure and similar acidity, the larger mesopore/external surface area of the hierarchical zeolite alters sharply the selectivity pattern. In other words, the enhanced accessibility of the acid sites for the hierarchical ZSM-5 sample promotes in a higher extent the alkylation reactions. This finding can be rationalized taking into account that, although in both cases metal and acid centers act in a cooperative way, for the first one Raney Ni possesses a more relevant role, being involved in most of the reactions shown in Figure 5, whereas the participation of the zeolite acid sites become predominant for the alkylation reactions.

The selectivity towards the main alkylphenols, obtained when using the h-ZSM-5 sample in the tandem system, is displayed in Figure 6.b). The main families were cresols, cyclohexylphenols and butylphenols, whose selectivities increased with the reaction temperature, reaching values of 36, 17 and 9% at 175°C, respectively. Within cresols and cyclohexylphenols, the main components were m-cresol and 2-cyclohexylphenol, respectively. The corresponding selectivities outperform those above attained with the tandem system employing n-ZSM-5. These results evidence the high potential of the tandem system Raney Ni + hierarchical ZSM-5 for the preparation of a variety of high added-value alkylphenols in the conversion of phenol/2-propanol.

1. **Conclusions**

The tandem system Raney Ni + ZSM-5 zeolite has been studied in the conversion of phenol assisted with 2-propanol, the latter being employed as both H-donor and alkylating agent. The results obtained show the strong influence of the zeolite accessibility, as well as of the reaction temperature on the product distribution.

When using the nanocrystalline zeolite sample (n-ZSM-5) in the tandem system, cyclohexene and benzene were the main products at low and intermediate temperatures (125 and 150°C), whereas the production of alkylphenols increased significantly with the reaction temperature. In the case of employing the hierarchical zeolite sample (h-ZSM-5) in combination with Raney Ni, their larger accessibility (higher mesopore/external area) enhanced the formation of alkylphenols, mainly cresols and cyclohexylphenols, their production being favored with the increase of the reaction temperature up to 175°C.

Two different reaction pathways co-exist in this system, leading to the formation of hydrocarbons and alkylphenols as main products, respectively. Although in both pathways metal and acid centers act in a cooperative way, for the first one Raney Ni possesses a more relevant role, whereas the participation of the zeolite acid sites becomes predominant in the formation of alkylphenols. Taking into account that most of the species involved in the latter are bulky compounds, the occurrence of a high accessibility in the zeolite catalyst is an essential factor for promoting this second pathway, as it occurs in the case of the hierarchical ZSM-5 sample.

The results here obtained indicate that a strong shift occurs in the predominant reaction pathway during the phenol/2-propanol conversion over the tandem Raney Ni + ZSM-5 system by modifying the reaction temperature and the accessibility of the zeolite, leading to obtain phenolics compounds with high-added value.

1. **Acknowledgements**

The authors want to thank the funding received by the Spanish Ministry of Economy, Industry and Competitiveness and the Spanish State Research Agency through the projects CTQ 2014-60209-R (CATPLASBIO) and CTQ2017-87001-R (BIOCASCHEM). Alba María García-Minguillán also thanks the Spanish government by her fellowship (BES-2015-075749) to perform the PhD in Rey Juan Carlos University.

**6. References**

(1) Li, C.; Zhao, X.; Huber, G. W.; Zhang, T. Catalytic transformation of lignin for the production of chemicals and fuels. *Chem. Rev.* **2015**, *115*, 11559.

(2) Serrano, D. P.; Melero, J. A.; Morales, G.; Iglesias, J.; Pizarro, P. Progress in the design of zeolite catalysts for biomass conversión into biofuels and bio-based chemicals*. Catal. Rev.* **2017**, *60*, 1.

(3) Shuttleworth, P. S.; De Bruyn, M.; Parker, H. L.; Hunt, A. J.; Budarin, V. L.; Matharu, A. S.; Clark, J. H. Applications of nanoparticles in biomass conversion to chemicals and fuels. *Green Chem.* **2014**,*16*, 573.

(4) Czernik, S.; Brigwater, A. V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **2004**,*18(2)*, 590.

(5) Mohan, D.; Pittnan, C. U.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* **2006**,*20*, 848.

(6) Hernando, H.; Fermoso, J.; Ochoa-Hernández, C.; Opanasenko, M.; Pizarro, P.; Coronado, J. M.; Čejka, J.; Serrano, D. P. Performance of MCM-22 zeolite for the catalytic fast pyrolysis of acid washed wheat straw. *Catal. Today* **2018**,*304*, 30.

(7) Jin, Y.; Yin, B.; Xia, Q.; Fang, T.; Shen, J.; Kuang, L.; Yang, C. Catalytic transfer hydrogenation of biomass-derived substrates to value-added chemicals on dual-function catalysts: opportunities and challenges. *ChemSusChem* **2019**,*12(1)*, 71.

(8) Li, Z.; Bi, Z.; Yan, L. Two-steps hydrogen transfer catalysis conversion of lignin to valuable small molecules compound. *Green Process. Synth.* **2017**, *6(4)*, 363.

(9) Ferrini, P.; Rinaldi, R. Catalytic biorefining of plant biomass to non pyrolytic lignin bio-oil and carbohydrates through hydrogen transfer reactions. *Angew. Chem. Int. Ed.* **2014**, *53*, 8634.

(10) Ferrini, P.; Rezende, C. A.;Rinaldi, R. Catalytic upstream biorefining through hydrogen transfer reaction: understanding the process from the pulp perspective. *ChemSusChem* **2016**,*9(22)*, 3171.

(11) Wang, X.; Rinaldi, R. Exploiting H-transfer reactions with Raney Ni for upgrade of phenolic and aromatic biorefinery feeds under unusual, low-severity conditions. *Energy Environ. Sci.* **2012**,*5*, 8244.

(12) Calvaruso, G., Burak, J. A., Clough, M. T.; Kennema, M.; Meemken, F.; Rinaldi, R. On the reactivity of dihydro-p-coumaryl alcohol towards reductive processes catalysed by Raney Nickel. *ChemCatChem* **2017**,*9(14)*, 2627.

(13) Chesi, C.; de Castro, I. B. D.; Clough, M. T.; Ferrini, P.; Rinaldi, R. The influence of hemicellulose sugars on product distribution of early-stage conversion of lignin oligomers catalysed by Raney Nickel. *ChemCatChem* **2016**, *8*, 2079.

(14) Kennema, M.; de Castro, I. B. D.; Meemken, F.; Rinaldi, R. Liquid phase H-transfer from 2-propanol to phenol on Raney Nickel: surface processes and inhibition. *ACS Catal*. **2017**, *7(4)*, 2437.

(15) Graça, I.; Woodward, R. T.; Kennema, M.; Rinaldi, R. Formation and fate of carboxylic acids in the lignin-first biorefining of lignocellulose via H-transfer catalysed by Raney Ni. *ACS Sustainable Chem. Eng.* **2018**, *6*, 13408.

(16) Barros Daltro de Castro, I.; Graça, I.; Rodríguez-García, L.; Kennema, M.; Rinaldi, R.; Meemken, F. Elucidating the reactivity of methoxyphenol positional isomers towards hydrogen-transfer reactions by ATR-IR spectroscopy of the liquid-solid interface of Raney Ni. *Catal. Sci. Technol.* **2018**,*8*, 3107.

(17) Geboers, J.; Wang, X.; Bruno de Carvalho, A.; Rinaldi, R. Densification of biorefinery schemes by H-transfer with Raney Ni and 2-propanol: A case study of a potential avenue for valorization of alkyl levulinates to alkyl γ-hydroxypentanoates and γ-valerolactone. *J. Mol. Catal. A* **2014** , *388 – 389*, 106.

(18) García, B.; Moreno, J.; Iglesias, J.; Melero, J. A. Transformation of glucose into sorbitol on Raney Nickel catalysts in the absence of molecular hydrogen: sugar disproportionation vs. Catalytic hydrogen transfer. *Top. Catal.* **2019**,*62(5-6)*, 570.

(19) Philippov, A. A.; Chibiryaev, A. M.; Martyanov, O. N. Raney Nickel catalysed hydrodeoxygenation and dearomatization under transfer hydrogenation conditions- reaction pathways of non-phenolic compounds. *Catal. Today* **2019** (in press), https://doi.org/10.1016/j.cattod.2019.05.033.

(20) Wang, H.; Rinaldi, R. A route for lignin and bio‐oil conversion: dehydroxylation of phenols into arenes by catalytic tandem reactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 11499.

(21) Jiang, Y.; Li, Z.; Tang, X.; Sun, Y.; Zeng, X.; Liu, S.; Lin, L. Depolymerization of cellulolytic enzyme lignin for the production of monomeric phenols over Raney Ni and acidic zeolite catalysts. *Energy Fuels* **2015**, *29*, 1662.

(22) Huang, Y.; Xia, S.; Ma, P. Effect of zeolite solid acids on the in situ hydrogenation of bio-derived phenol. *Catal. Commun*. **2017**, *89*, 111.

(23) Přech, J.; Pizarro, P.; Serrano, D. P.; Čejka, J. From 3D to 2D zeolite catalytic materials. *Chem. Soc. Rev.* **2018**, *47(22)*, 8263.

(24) Nandiwale, K. Y.; Bokade, V. V. Selective synthesis of propofol (2, 6-diisopropylphenol), an intravenous anesthetic drug, by isopropylation of phenol over H-beta and H-mordenite. *RSC Adv*. **2014**, *4*, 32467.

(25) Amandi, R.; Scovell, K.; Licence, P.; Lotz, T. J.; Poliakoff, M. The synthesis of o-cyclohexylphenol in supercritical carbon dioxide: towards a continuous two-step reaction. *Green Chem*. **2007**, *9*, 797.

(26) Meyer, B. K.; Ni, A.; Hu, B.; Shi, L. The synthesis of o-cyclohexylphenol in supercritical carbon dioxide: towards a continuous two-step reaction. *J. Pharm. Sci*. **2007**, *96*, 3155.

(27) Serrano, D. P.; Aguado, J.; Escola, J. M.; Rodríguez, J. M.; Peral, A. Hierarchical zeolites with enhanced textural and catalytic properties synthesized from organofunctionalized seeds. *Chem. Mater*. **2006**, *18(10)*, 2462.

(28) Serrano, D. P.; Aguado, J.; Escola, J. M.; Rodríguez, J. M.; Peral, A. Effect of the organic moiety nature on the synthesis of hierarchical ZSM-5 from silanized protozeolitic units. *J. Mat. Chem*. **2008**, *18*, 4210.

(29) Abelló, S.; Bonilla, A.; Pérez Ramírez, J. Mesoporous ZSM-5 zeolite catalysts prepared by desilication with organic hydroxides and comparison with NaOH leaching. *Appl. Catal. A* **2009**, *364*, 191.

(30) Ogura, M.; Shinomiya, S.; Tateno, J.; Nora, Y.; Kikuchi, E.; Matsukata, M. Formation of Uniform Mesopores in ZSM-5 Zeolite through Treatment in Alkaline Solution. *Chem. Lett*. **2000**, *29(8)*, 882.

(31) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87(9)*, 1.

(32) Choi, M.; Cho, H. S.; Srivastava, R.; Venkatesan, C.; Choi, D. H.; Ryoo, R. Amphiphilic organosilane-directed synthesis of crystalline zeolite with tunable mesoporosity. *Nature Mater*. **2006**, *5*, 718.

(33) Verboekend, D.; Pérez Ramírez, J. Desilication mechanism revisited: highly mesoporous all‐silica zeolites enabled through pore‐directing agents. *Chem. Eur*. **2011**, *17*, 1137.

(34) Engelhardt, G. Solid-state NMR spectroscopy applied to zeolites. *Stud. Surf. Sci. Catal*. **2001**, *137*, 387.

(35) Berenguer, A.; Sankaranarayanan, T. M.; Gómez, G.; Moreno, I.; Coronado, J. M.; Pizarro, P.; Serrano, D. P. Evaluation of transition metal phosphides supported on ordered mesoporous materials as catalysts for phenol hydrodeoxygenation. *Green Chem*. **2016**, *18*, 1938.

(36) Mullen, C. A.; Tarves, P. C.; Boateng, A. A. Role of potassium exchange in catalytic pyrolysis of biomass over ZSM-5: formation of alkyl phenols and furans. *ACS Sustain. Chem. Eng*. **2017**, *5*, 2154.

(37) Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*, John Wiley & Sons, 1995.

(38) Zhao, C.; Kou, Y.; Lemonidou, A. A.; Li, X.; Lercher, J. A. Hydrodeoxygenation of bio-derived phenols to hydrocarbonsusing RANEY® Ni and Nafion/SiO2 catalysts. *Chem. Commun*. **2010**, *46*, 412.

(39) Zhao, Z.; Shi, H.; Wan, C.; Hu, M. Y.; Liu, Y.; Mei, D.; Camaioni, D. M.; Hu, J. Z.; Lercher, J. A. Mechanism of phenol alkylation in zeolite H-BEA using in situ solid-state NMR spectroscopy. *J. Am. Chem. Soc*. **2017**, *27*, 9178.

**FIGURE CAPTIONS**

**Figure 1.** a) XRD patterns and b) Ar adsorption-desorption isotherms at -186.15 ºC of the n-ZSM-5 and h-ZSM-5 zeolites.

**Figure 2.** TEM micrographs of n-ZSM-5 and h-ZSM-5 zeolites.

**Figure 3.** 27Al MAS NMR spectra of the n-ZSM-5 and h-ZSM-5 zeolites.

**Figure 4.** Phenol/2-propanol conversion over Raney Ni + n-ZSM-5: a) Phenol conversion and product distribution, b) Selectivity towards phenolics.

**Figure 5**. Phenol/2-propanol conversion over the tandem system Raney Ni + ZSM-5: pathway leading to hydrocarbons as main products (favored at low temperature).

**Figure 6**. Phenol/2-propanol conversion over Raney Ni + h-ZSM-5: a) Conversion and product distribution, b) Selectivity towards phenolics.

**Table 1. Physicochemical properties of the zeolites**

|  |  |  |
| --- | --- | --- |
| **Property** | **n-ZSM-5** | **h-ZSM-5** |
| BET surface area (m2/g)1 | 405 | 562 |
| Total pore volume (cm3/g)1 | 0.45 | 0.53 |
| Micropore surface area (m2/g)1 | 277 | 289 |
| External+mesopore surface area (m2/g)1 | 128 | 273 |
| Micro/mesopore mean diameter (nm) | 0.55 | 0.55/3.4 |
| Tmax (ºC)2 | 350 | 357 |
| Total acidity(mmol NH3 /g)2 | 0.35 | 0.31 |
| Si/Al atomic ratio | 30 | 32 |

1 determined from the Ar adsorption-desorption isotherms at -186.15 ºC

2 calculated by NH3 TPD measurements

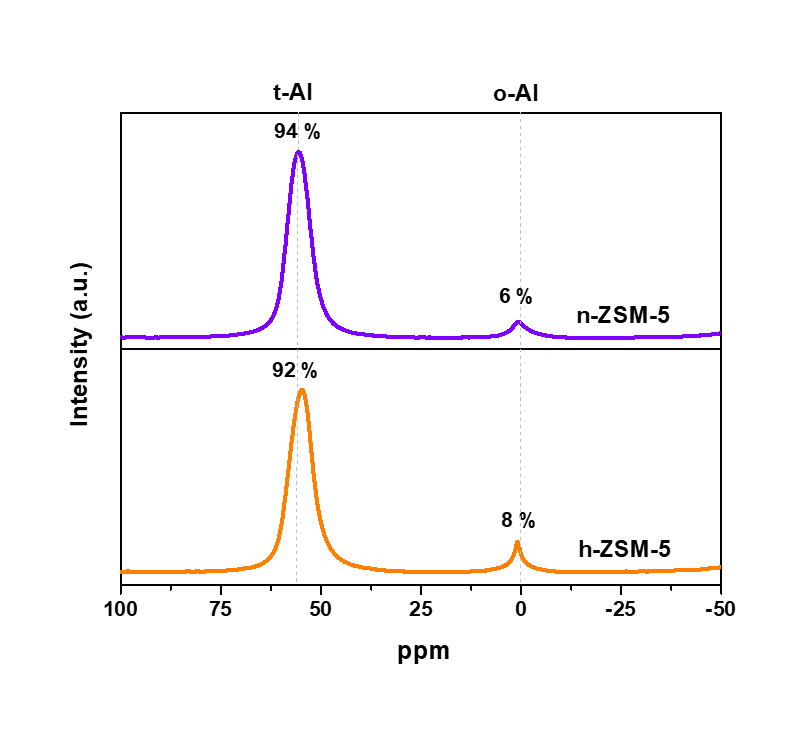
**FIGURE 1**

****

**FIGURE 2**

**C:\Users\josemaria.escola.sae\Documents\articulos\paperalba2\version final\Figura 2.tiff**

**FIGURE 3**

****

**FIGURE 4**



**FIGURE 5**



**H-T:** Hydrogen Transfer

**A-D:** Acid Dehydration

**FIGURE 6**

