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# Zeolite-Beta-supported platinum catalysts for hydrogenation/hydrodeoxygenation of pyrolysis oil model compounds

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ABSTRACT

Phenol, cresols, guaiacol and eugenol were studied to describe the effect of substituent position and type on the reactivity of these phenolic compounds. Conversion of cresols under deoxygenation/hydrogenation reactivities increased in order m- > o- > p-cresol over Pt/Beta zeolite with Si/Al = 12.7 and o- > m- > p-cresol over the Pt/Beta with lower Al content (Si/Al = 20.7). Major products of cresols hydrogenation were methyl cyclohexanols. Phenol was converted into a mixture of cyclohexane, cyclohexanol and cyclohexanone. An increase in Si/Al ratio of the parent zeolite-based catalysts resulted in a decrease in the overall conversion of cresols and phenol. On the other hand, an increase in Si/Al ratio of catalysts prepared by dealumination led to accelerated conversion of phenol to cyclohexane. Using the lab-prepared mesoporous Beta catalyst with a comparable Si/Al ratio to the commercial one (ca. 20), higher yields of cyclohexanol were obtained in conversion of phenol.

## 1. Introduction

Lignocellulose is the most abundant renewable source of chemicals. While cellulose is primarily used for pulp and paper production ($5–36 \times 10^8$ tons/year [1]), it can be also hydrolyzed to fermentable sugars that can be either fermented to produce ethanol or butanol, or transformed for instance by hydrogenation or dehydration to yield intermediates for chemical syntheses [2–7]. A similar strategy relying on initial hydrolysis can be also adopted for upgrading of hemicelluloses [5,8]. On the other hand, the chemical nature of lignin differs significantly from cellulose and hemicelluloses and different strategies for its upgrading need to be employed [9,10]. In addition, the origin of lignocellulosic biomass plays an important role in selecting the most suitable upgrading technology. For instance, large scale pulping or derived technologies are suitable for wood processing [11], while agricultural residues, such as straw, might require the use of pyrolysis technologies in order to enhance the volumetric energy density (the volumetric energy density of a straw bale is only 2 GJ/$m^3$) and make the transport to an upgrading facility economically feasible [12].

Particularly wood is being exploited in millions of cubic meters for pulp, paper and ethanol production. Together with agricultural residuals (straw), which can be transformed into ethanol using hydrolysis method, waste materials from pulp and paper production can become important source of chemicals. These materials are usually used traditionally for process heat recovery (lignin burning). Lignin, typically formed by methoxy-substituted phenyl propanoid units (basic precursors: sinapyl alcohol, coniferyl alcohol and p-coumaryl alcohol) is a potential source for gasoline and special chemicals production [9].

Thermal or so-called catalytic pyrolysis makes possible the transformation of solid lignin or lignocellulose into a liquid phase that can be processed much more easily by industrial catalytic technologies [13–15]. Typically, the liquid products consist of phenolic compounds (originating from lignin), various acids, aldehydes and ketones (attributable to cellulose and hemicelluloses), and water. The exact composition of pyrolysis oil depends on feedstock composition and reaction (pyrolysis) conditions, such as temperature, residence time or catalyst presence [16]. In particular phenolics present in pyrolysis oils are interesting compounds for subsequent hydrothermal processing (upgrading) as potential fuel and renewable chemicals sources. Due to a high reactivity of pyrolysis oil, i.e. their tendency to polymerize under increased temperature conditions, pyrolysis oils have to be generally stabilized first, e.g. by mild hydrotreating [17–20].

Consequently, large attention is focused on transformation of relevant model compounds. For instance, many studies were focused on hydrothermal conversion of phenol. This model compound can be deoxygenated over sulfided NiMo and CoMo catalysts [21]. Typical reaction pathway described for phenol conversions encompasses parallel and consecutive reactions, e.g. hydrodeoxygenation of hydroxyl group (benzene formation) followed by

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aromatic ring hydrogenation (cyclohexane) [22]. Alternatively, the aromatic ring can be hydrogenated first followed by cyclohexanol dehydration and subsequent hydrogenation of the resulting cyclohexene to cyclohexane [22]. Sulfided catalysts are able to transform phenol at temperatures around 250 °C. Their disadvantage is the contact with sulfur and possible product contamination, because of sulfur removal from active sites during the reaction [23]. Moreover, sulfur needs to be continuously replenished otherwise the catalyst will be desulfided and lose gradually its activity In addition the presence of sulfur-containing compounds has a negative impact on the reaction rate of deoxygenation due to competitive adsorption of sulfur- and oxygen-containing compounds.

Presence of water, which is a typical component of pyrolysis oils (water content in pyrolysis oil can reach up to approx. 30 wt.% [24]), can also negatively affect catalytic activity. Nevertheless, the deactivation caused by water is not as severe as in case of ammonia and hydrogen sulfide [23,25].

Nickel and molybdenum oxides were described as suitable catalysts for deoxygenation of alkyl and methoxyphenols [26]. Alumina-supported NiMo oxide catalyst (3% NiO, 15% $MoO_3$) was found to deoxygenate and hydrogenate dihydroxybenzenes, cresols and guaiacol at temperatures between 350 and 500 °C. Dihydroxybenzenes were predominantly converted into phenol (ortho isomer) and products with saturated ring (meta and para isomers), cresols were converted to toluene, dimethylbenzenes and methyl cyclohexane. Guaiacol was transformed into a mixture of phenol, benzene, toluene and cyclohexane. The yields of benzene and toluene increased with increasing reaction temperature. $Pt/Al_2O_3$ (1 wt.% of Pt) catalyst was reported to convert guaiacol at 300 °C into phenol, catechol and methylcatechol without ring saturation [27]. In comparison with $Pt/Al_2O_3$ (1 wt.% of Pt), higher guaiacol conversion can be obtained at the same reaction conditions with HY zeolite without platinum [27], in both cases, catechols and dihydroxybenzenes were described as main products, other detected products were identified as methyl guaiacols. On the other hand, selective conversion of phenol to cyclohexanol was described over Pd/C catalyst at a relatively low temperature 80 °C. Cyclohexanone was detected as a reaction intermediate [28].

Because of their crystalline structure and defined pore shapes and sizes, zeolites are interesting catalyst supports as they allow tuning catalytic properties and performance. Platinum is well-known as highly active metal for hydrogenation reactions at significantly lower temperatures than for example sulfided catalysts. Hence zeolite Beta, having large pores formed by 12 rings [29], was selected for low temperature transformation of pyrolysis oil model compounds. The following phenolic model compounds were selected to study the effects of the substituent types and their mutual positions: phenol, o-, m- and p-cresols, guaiacol and eugenol. Apart from studying the effects of substituents on hydrogenation and deoxygenation, the influence of catalyst properties (Si/Al ratio, porosity) and reaction conditions on catalyst activities and selectivities were investigated as well.

## 2. Experimental

### 2.1. Catalysts

Two commercial zeolites Beta (Zeolyst, CP 814E and CP 814C) were used for studying the effect of Si/Al ratio on phenol and cresols hydrogenation. They were denoted as Z-20 (CP 814 E; Si/Al = 12.7) and Z-23 (CP 814C; Si/Al = 20.7). The Z-20 zeolite Beta has been dealuminated using 1 M hydrochloric acid for 15 min at laboratory temperature to obtain zeolite Beta with a similar Si/Al ratio to that of Z-23. The dealuminated zeolite Beta was denoted Z-20D and had Si/Al ratio equals to 21.5 as determined by XRF analysis. According to literature, only non-skeletal aluminum should be removed at these conditions [30]. The last support used in the study was mesoporous zeolite Beta prepared in VUAnCh and denoted 3MF (Si/Al = 10.4, specific surface area 602 $m^2/g$, micropores volume 0.155 $cm^3/g$, mesopores volume 0.361 $cm^3/g$, medium pore diameter 3.7 nm). The sample 3MF was prepared in a 5 l autoclave by hydrothermal synthesis with tetramethylammoniumhydroxide as a template. A secondary template, a renewable raw material, enabling formation of mesopores during hydrothermal synthesis was used (for details see [31]). The removal of this template during calcination led to creation of mesopores in the structure.

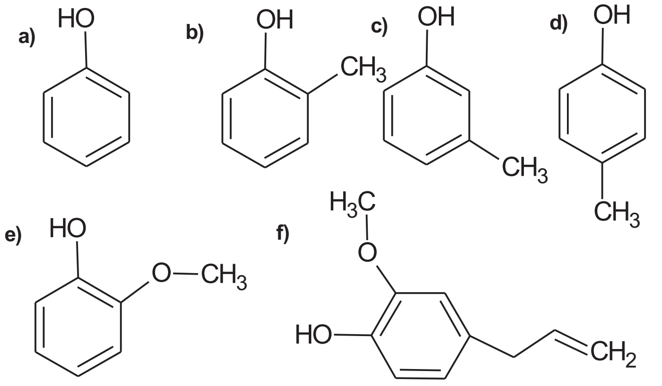

**Fig. 1.** Model compounds used in the hydrogenation/deoxygenation study: (a) phenol, (b) o-cresol, (c) m-cresol, (d) p-cresol, (e) guaiacol, and (f) eugenol.

Zeolites were then impregnated by tetraammineplatinum(II)nitrate to obtain catalyst with Pt content of 0.5 wt.%. The impregnation was performed by a conventional impregnation method using aqueous solution of the precursor. The support was suspended in the aqueous solution of $[Pt(NH_3)_4](NO_3)_2$ and stirred in a rotator–evaporator for 1 h. Then the solution was heated under constant stirring until evaporated to dryness. After impregnation, the samples were dried at 120 °C for 1 h.

### 2.2. Chemicals

Phenol (S. Aldrich, >98%), o-cresol (S. Aldrich, >98%), m-cresol (S. Aldrich, >98%) and p-cresol (S. Aldrich, >98%), guaiacol (S. Aldrich, >98%) and eugenol (S. Aldrich, >98%) were used as lignin pyrolysis oil model compounds (Fig. 1) for hydrodeoxygenation/hydrogenation experiments. Hydrogen was supplied by Air Products (99.9%). Isooctane (>98%) was supplied by Lachner Chemicals.

### 2.3. Catalyst characterization

Si/Al ratios of the four zeolite Beta samples were obtained using XRF analysis (Table 1). The same method was also used to confirm Pt concentration on the catalysts (Table 1). Specific surface was determined using nitrogen physisorption using BET and Dubinin calculation methods (Table 2). Catalyst acidity was measured with FTIR/pyridine adsorption (Table 3). Distributions of catalyst particle

**Table 1**
Si/Al ratios and platinum content measured using XRF technique and platinum dispersion with platinum particle diameter – $p_D$ (by CO chemisorption).

| Catalyst | Si/Al | Pt (wt.%) | Pt dispersion (%) | $p_D$ (nm) |
|---|---|---|---|---|
| Pt/Z-20 | 12.7 | 0.50 | 20.6 | 5.5 |
| Pt-Z-23 | 20.7 | 0.48 | 15.5 | 7.3 |
| Pt/3MF | 10.4 | 0.48 | 34.6 | 3.3 |
| Pt/Z-20D | 21.5 | 0.43 | 11.4 | 9.9 |

**Table 2**
Specific surface areas of catalysts.

| Catalyst | Specific surface area (BET) ($m^2/g$) | Specific surface area (Dubinin) ($m^2/g$) | Micropore volume ($cm^3/g$) |
|---|---|---|---|
| Pt/Z-20 | 514 | 751 | 0.267 |
| Pt/Z-20D | 548 | 788 | 0.280 |
| Pt/Z-23 | 539 | 879 | 0.312 |
| Pt/3MF | 508 | 722 | 0.256 |

**Table 3**
Brønsted (B) and Lewis (L) sites concentration determined by FTIR/pyridine adsorption followed by desorption at 200 °C ($C_B$ concentration of Brønsted sites, $C_L$ concentration of Lewis sites, and $C_{Al}$ concentration of aluminum in structure was determined from concentration of acid sites).

| Catalyst | $C_{Al}$ (mmol/g) | $C_B$ (mmol/g) | $C_L$ (mmol/g) | $C_B$ (%) | $C_L$ (%) |
|---|---|---|---|---|---|
| Pt/Z-20D | 0.40 | 0.16 | 0.12 | 57 | 43 |
| Pt/Z-20 | 0.55 | 0.24 | 0.16 | 60 | 40 |
| Pt/Z-23 | 0.40 | 0.20 | 0.10 | 66 | 34 |
| Pt/3MF[a] | 0.33 | 0.19 | 0.07 | 72 | 28 |

[a] Catalyst activation prior pyridine adsorption at 400 °C, the other catalysts were activated only at 200 °C.

sizes were analyzed using laser scattering method (Mastersizer 2000) and the values are reported in Table 4.

### 2.4. Experiments

Hydrogenation/deoxygenation experiments were carried out in a 500 ml batch stirred reactor (PPI). The reactor vessel was filled with 1.00 g of not calcined catalyst and flushed with nitrogen and hydrogen. Before each experiment, catalyst was heated at 200 °C in presence of hydrogen. After reactor cooling to ambient temperature, the vessel was filled with 300 ml of isooctane containing 0.125 mol of substrate. Reactor free space was gradually flushed first with nitrogen and then with hydrogen and pressurized to 1 MPa. Reactor was then heated under slow stirring (less than 50 rpm) for promoting heat transfer until the desired reaction temperature (180 °C) was reached. After reaching the reaction temperature, hydrogen pressure was set at 5 MPa and the stirrer rotation was increased to 1500 rpm. The reaction was carried out under the set reaction conditions for 90 min. Samples of reaction products were taken at defined reaction times and analyzed off-line by GC. As constant amount of reactant and catalyst were used in each experiment, the determined conversions correspond to catalyst activity, i.e. rate of disappearance of reactant per mass of catalyst.

For catalyst activity study, o-, m- and p-cresols were used for studying the effect of isomer type, i.e. of the methyl position relative to the hydroxyl group, on substrate hydrogenation and deoxygenation. Eugenol was used as a model compound for pyrolysis oil stabilization (allyl hydrogenation). Guaiacol represents a model compound for studying the effect of methoxy substitution that is typical in products of lignin pyrolysis. Samples of products and substrates were analyzed by gas chromatography, using HP-PONA column with temperature ramp starting at 35 °C for 15 min and 5 °C/min up to 250 °C.

**Table 4**
Catalyst mean particle size.

| Catalyst particle size (μm) | | | |
|---|---|---|---|
| Pt/Z-20 | Pt/Z-23 | Pt/Z-20D | Pt/3MF |
| 10.20 | 2.79 | 13.20 | 72.82 |

## 3. Results and discussion

Direct comparison of catalysts for phenol hydrogenation and deoxygenation is depicted in Fig. 2. The comparison of two parent zeolites Beta (Z-20, Z-23) modified with platinum reveals a higher catalytic activity of Pt/Z-23 with higher Si/Al ratio and hence lower Brønsted as well as Lewis acidity (Table 3), as compared with Pt/Z-20. As both catalysts have the same Pt content (Table 1), the difference could be attributed to the smaller size of zeolite crystal aggregates of Pt/Z-23 (2.8 vs. 10.2 μm, Table 4), i.e. a better accessibility of active sites in Pt/Z-20. Furthermore, Pt/Z-23 has also a higher specific surface area than Pt/Z-20 (Table 2). The mild dealumination of Z-20 resulted in a significantly increased activity of the Pt/Z-20D catalyst as it afforded virtually complete phenol conversion in less than 15 min (Fig. 2). The physico-chemical data are comparable with Pt/Z-23 and thus do not provide a clear evidence of the cause of this substantial improvement, but it could be plausibly explained by partial removal of aluminum due to dealumination, particularly in extra framework positions [30], and hence improved mass transfer of phenol in the pore structure. On the other hand, the mesoporous Beta (Pt/3MF) exhibits catalytic activity comparable with Pt/Z-20 (Fig. 2) even though the lowest mass transfer limitations can be expected due to the mesoporosity. However, as can be seen in Table 4, the mean catalyst particle size exceeds dramatically the size of the other three catalysts (72.8 vs. <15 μm) and could be the reason for the apparently lower catalyst activity. Moreover, it can be observed that the initial catalytic activity (Fig. 2) is lower for the catalysts with Si/Al ratio 10–12 than for those with Si/Al ratio about 20–22 (Table 1). This might indicate that low acidity of a catalyst is preferred. The Pt dispersion (Table 1) shows that the particle size of Pt crystallites might have an impact on the observed conversion as well. However, there is no obvious correlation between the Pt dispersion on the one hand and phenol conversion on the other hand. In fact, the highest phenol conversion after 20 min was observed over Pt/Z-20D having the lowest dispersion (Fig. 2), while the lowest conversion after the same time was found when using the parent zeolite (Pt/Z-20) having the second lowest Pt dispersion (Table 1).

In terms of selectivity, discernible differences can be found among the zeolite-Beta-based platinum catalysts. Three main products were observed that can be classified as hydrogenation products (cyclohexanone and cyclohexanol) and a deoxygenation product (cyclohexane). The other plausible deoxygenation product, benzene, was detected only in trace amounts (<0.1%). The presence of cyclohexanone in product samples and particularly the cyclohexanone yield profile (Fig. 2C) as a function of reaction time or conversion indicate reaction pathway of ring saturation with a parallel hydroxyl group into ketone change, i.e. cyclohexenol to cyclohexanone rearrangement (Fig. 3). The same reaction pathway has been described for phenol conversion over sulfided catalysts [21]. The results indicate that cyclohexane is a product of cyclohexanol deoxygenation, i.e. dehydration over acid sites followed by hydrogenation of the olefin formed as suggested recently by Lercher and coworkers [32], rather than benzene hydrogenation (direct hydrodeoxygenation is a plausible pathway, but not a significant one in the case of phenol deoxygenation).

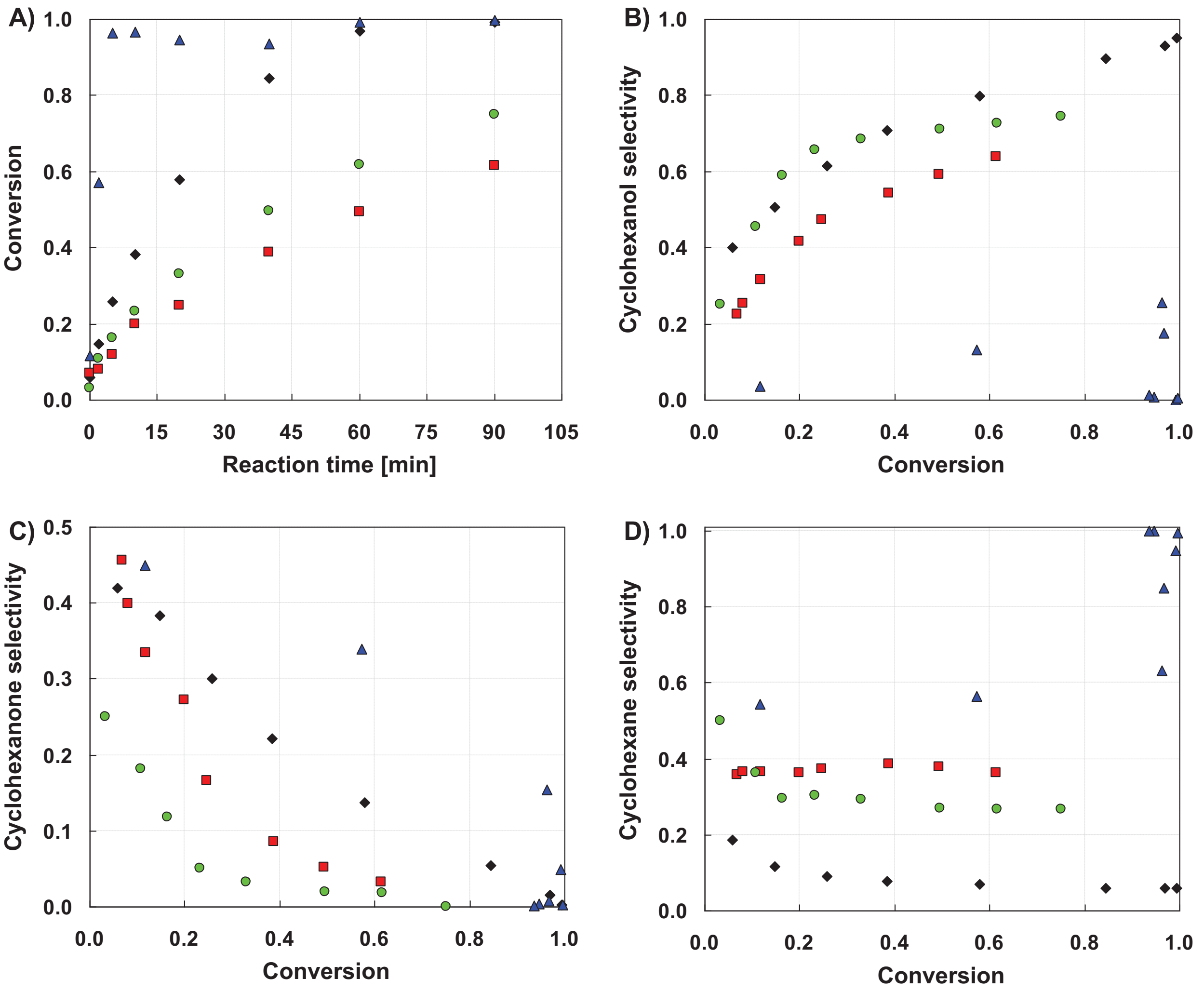

**Fig. 2.** Conversion (A) and selectivities to cyclohexanol (B), cyclohexanone (C) and cyclohexane (D) over Pt/Z-23 (♦) and Pt/Z-20 (🟥), Pt/Z-20D (▲) and Pt/3MF (●).

The high initial selectivity to cyclohexane (at ca. 5% conversion about 40%), which is the ultimate product of phenol hydrogenation and deoxygenation is rather surprising and can be attributed to quick initial deactivation of the most active deoxygenation sites (Fig. 2D). Cyclohexanol was the main reaction product for all the Pt/Beta catalysts, but Pt/Z-20D, which yielded almost exclusively cyclohexane.

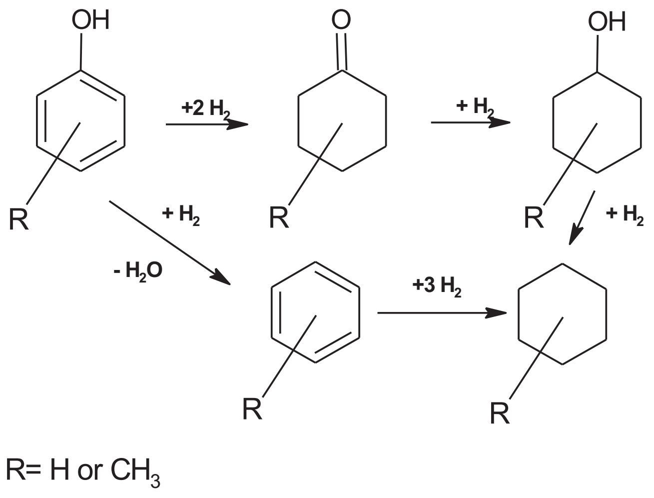

**Fig. 3.** Reaction pathways leading to (alkyl)naphthenes from (alkyl)phenols.

The deoxygenation level (calculated as relative oxygen content decrease; based on product composition) increased gradually with increasing phenol conversion for all tested catalysts (Fig. 4). Pt/Z-23 converted phenol almost exclusively into cyclohexanol, deoxygenation selectivity at 60% conversion was ca. 6%. The lower Al content of Pt/Z-23, i.e. lower concentration of Brønsted and Lewis acid sites (Table 3), resulted in very low deoxygenation selectivity in comparison with Pt/Z-20 over the whole conversion range (ca. 10 vs. ca. 40%). The deoxygenation level did not exceed 15% in the case of Pt/Z-23 even at complete conversion of phenol (Fig. 4). On the contrary, the data in Fig. 2D demonstrate that Pt/Z-20 exhibited fairly stable formation of cyclohexane over the whole range of achieved conversions over this catalyst (0–60%). This can be attributed to the higher acidity of Pt/Z-20 in comparison with Pt/Z-23 together with the larger size of zeolite crystal aggregates. Due to a higher diffusional resistance the secondary reactions (i.e. deoxygenation of cyclohexanol to cyclohexane) would be preferred over the primary ones (i.e. aromatic ring saturation). This conclusion is further supported by the lower concentration of cyclohexanone in the product mixture over Pt/Z-20 in comparison with Pt/Z-23 at comparable phenol conversion, e.g. 4% vs. 13% at 60% conversion (Fig. 2C).

Dealumination of Z-20 causing an increase in Si/Al ratio (Table 1) to a similar value of Si/Al as the one of Pt/Z-23 resulted in faster ring hydrogenation accompanied by high deoxygenation activity

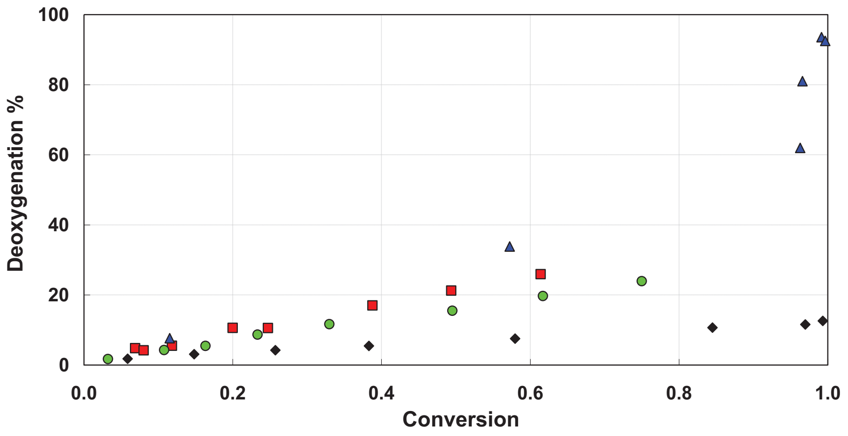

**Fig. 4.** Relative deoxygenation as function of phenol conversion. Pt/Z-23 (♦) and Pt/Z-20 (🟥), Pt/Z-20D (▲) and Pt/3MF (●).

(Fig. 2). As a result of dealumination slight specific surface area increase (Table 2) and decrease in concentration of Brønsted and Lewis acid sites (Table 3) in comparison with the parent material were observed. Despite the final values are relatively similar to those of Pt/Z-23, Pt/Z-20D outperformed Pt/Z-23 both in terms of activity and selectivity. In particular a striking difference was observed in selectivity as at complete conversion Pt/Z-23 yielded almost exclusively cyclohexanol (selectivity > 95%), while Pt/Z-20D afforded only cyclohexane. Such a difference cannot be explained by the relatively minor differences in acidity and can be thus attributed to higher porosity of the dealuminated catalyst resulting in better accessibility of active centers.

Platinum supported on the in-house prepared mesoporous zeolite Beta support (Pt/3MF) with 75% conversion after 90 min of reaction (Fig. 2A) exhibited a medium hydrogenation activity in comparison with Pt/Z-23 (99% conversion) and Pt/Z-20 (61% conversion). It also showed a higher ring hydrogenation activity than Pt/Z-23 and a higher deoxygenation activity than Pt/Z-20. Based on its physico-chemical properties, a performance closer to the Pt/Z-20D catalyst would be expected. The significant difference from this catalyst can be most probably assigned to the dramatically larger size of catalyst particles and the resulting diffusion limitation effects (72.8 vs. <15 μm, Table 4).

The effect of o-, m- and p-substitution on hydrogenation and deoxygenation activity of zeolite-Beta-supported platinum catalysts was studied using individual cresol isomers. The reactivity of cresol isomers decreased in the order m- > o- > p- over Pt/Z-23 (Fig. 5). In general, the reactivity of cresols was lower over Pt/Z-23 and Pt/Z-20 than the reactivity of phenol. Predominant reaction products were the corresponding methylcyclohexanols and methylcyclohexanones. In contrast to phenol conversion, direct hydrodeoxygenation yielding toluene was observed in addition to the aromatic ring hydrogenation (Fig. 6). The selectivity to toluene was pronounced particularly at low conversions suggesting that this reaction pathway is parallel to the hydrogenation route and the active centers might be quickly deactivated. Toluene formation can be explained as result direct hydrodeoxygenation without aromatic ring hydrogenation as described in literature for high temperature conversion over aluminum supported catalysts [21,26]. The difference between cresols and phenol could be attributed to the presence of methyl substituent, which makes the carbon–oxygen bond weaker and facilitates thus its rupture, i.e. direct deoxygenation. Moreover, the electronic effects of the methyl substituent are further reflected in the initial selectivities to toluene. The lowest selectivity to toluene was observed in the case of m-cresol (Fig. 6), where the methyl substituent has a weaker electronic effect on the hydroxyl group than the methyl substituent in p- or o-position. The lower initial selectivity to toluene in o-cresol deoxygenation (in comparison with p-cresol) can be attributed to steric effects affecting the adsorption of o-cresol, but not of p-cresol (Fig. 6).

Only insignificant amounts of the ultimate product, i.e. methylcyclohexane, were obtained. This indicates that hydrogenation of toluene was very limited. Moreover, it also suggests that methylcyclohexanols were not deoxygenated to afford methylcyclohexane. Similar behavior over Pt/Z-23 was observed also for phenol as it yielded predominantly cyclohexanol. While Pt/Z-20 showed higher

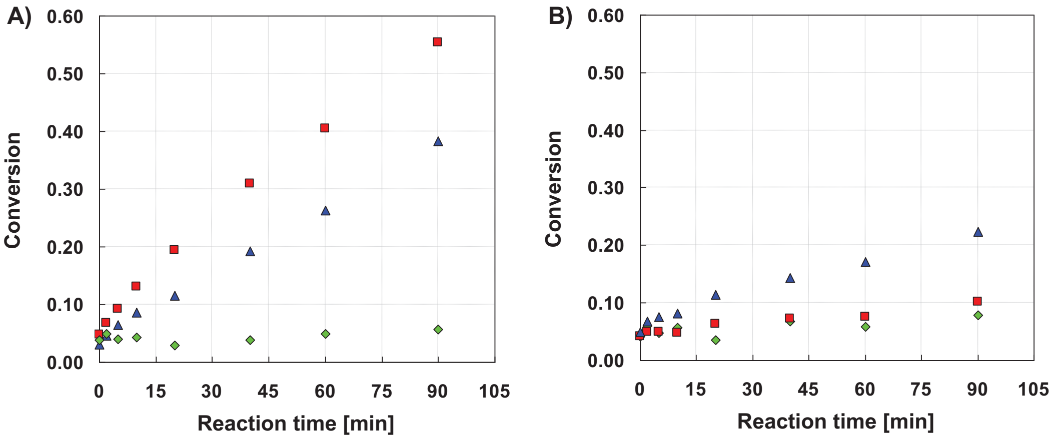

**Fig. 5.** Effect of methyl position on compound reactivity (A) (Pt/Z-23); (◆) p-cresol, (🟥) m-cresol, (▲) o-cresol and conversion into methylcyclohexanols (B).

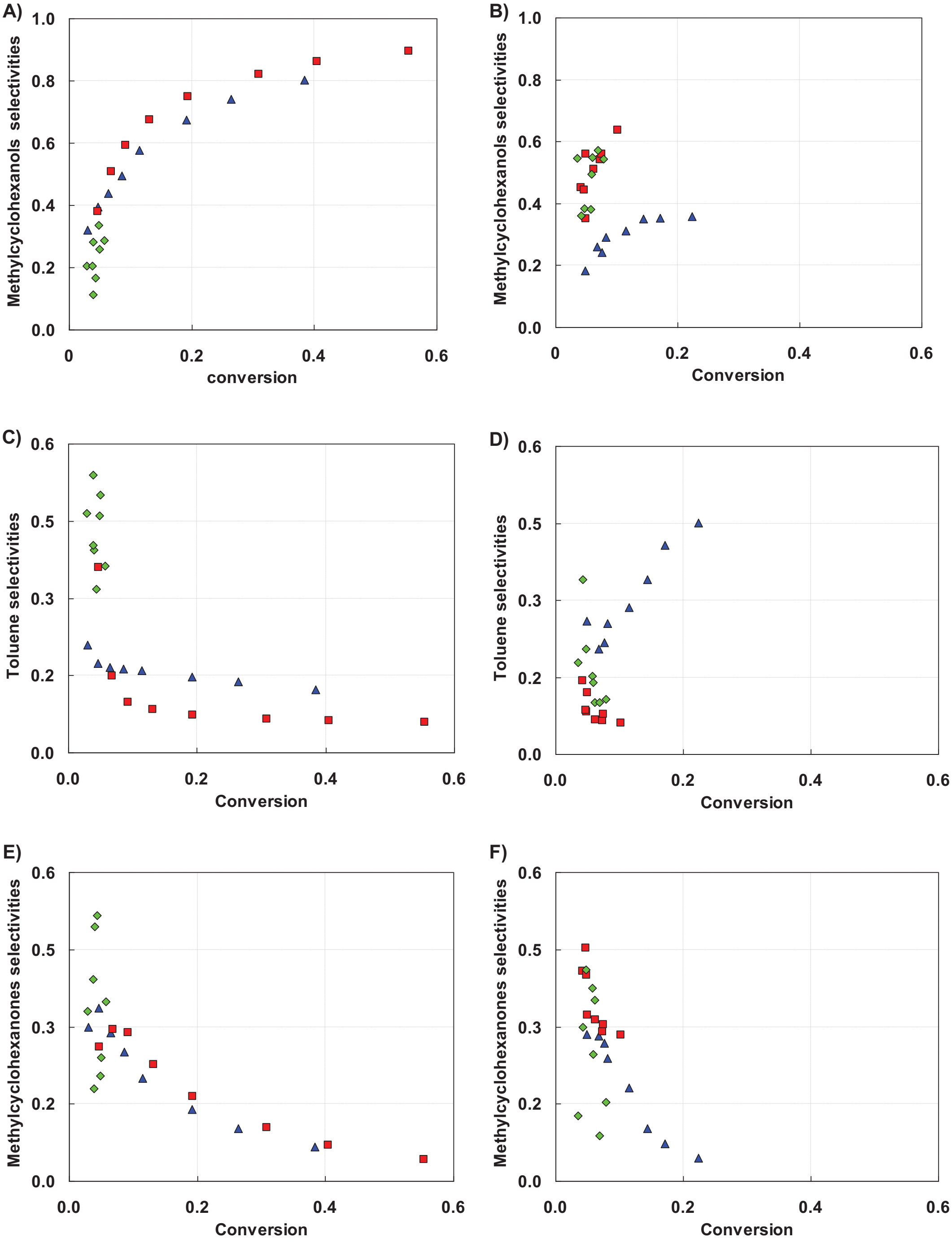

**Fig. 6.** Effect of methyl position on selectivity to methylcyclohexanol over Pt/Z-23 (A) and Pt/Z-20 (B), to toluene over Pt/Z-23 (C) and Pt/Z-20 (D), and to methylcyclohexanones over Pt/Z-23 (E) and Pt/Z-20 (F). Feedstocks: (◆ ) p-cresol, (■ ) m-cresol, and (▲ ) o-cresol.

selectivity to deoxygenation products in the case of phenol, the same was not observed in the case of cresols. However, their conversions were rather low ca. 10%. Using the analogy with phenol hydrodeoxygenation discussed above, it can be assumed that the ketones were formed along a similar pathway as cyclohexanone from phenol. This is supported by the experimental data.

The comparison of phenol and guaiacol over Pt/Z-23 has shown an important stabilization effect of the methoxy group substitution for deoxygenation, as the only detected product was 2-methoxycyclohexanol. Moreover, the ring hydrogenation was significantly suppressed by the methoxy group in comparison with phenol (no substitution) and o-cresol (methyl substitution) as depicted in Fig. 7. Presence of another substituent on aromatic ring hinders the aromatic ring saturation due to affecting its adsorption on active Pt sites. At the same time, deoxygenation rate is also affected and with increasing substituent molecular weight lower deoxygenation level can be awaited. Crucial for reactivity of differently substituted phenols in Pt-modified zeolites are adsorption modes and transport parameters affected by their molecular dimensions. Estimates of the maximum molecular dimension (kinetic diameter) of the investigated model compounds are given in Table 5. Molecule size effect on aromatic ring hydrogenation can be important particularly in zeolites. The maximum diameter ($d_{\max}$) increases in the order phenol < o-cresol < guaiacol

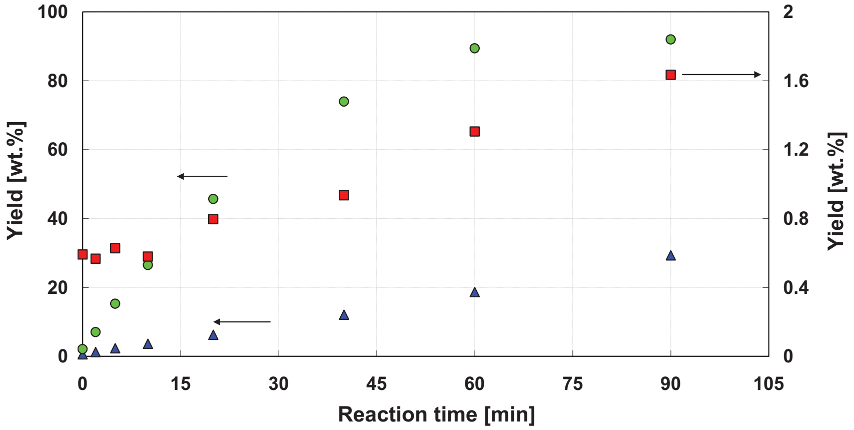

**Fig. 7.** Aromatic ring hydrogenation affected by 2-phenol substitution, (● ) cyclohexanol (from phenol), (▲ ) 2-methylcyclohexanol (+methyl substitution, from o-cresol) (■ ) 2-methoxycyclohexanol (+methoxy group, from guaiacol).

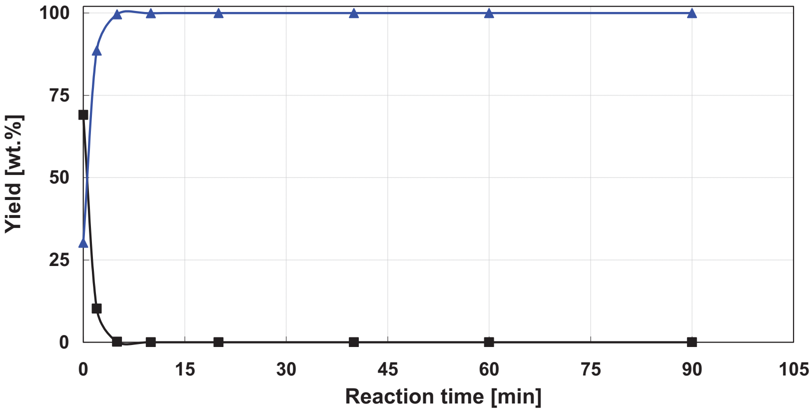

**Fig. 8.** Allyl group hydrogenation (eugenol (■) to 2-methoxy-4-propylphenol (▲ ))).

which agrees with their observed reactivity, i.e. the reactivity over Pt/Z-23 decreased with the increasing molecule diameter ($d_{max}$). The increasing molecule diameter affects the mobility of molecules in catalyst pores.

Stabilization of allyl groups of methoxy compounds, such as eugenol is essential for pyrolysis oil stabilization before its hydrogenation/deoxygenation treatment. In agreement with the experiments performed with guaiacol the aromatic ring of eugenol was not hydrogenated over Pt/Z-23. Only the allyl group was hydrogenated to yield 2-methoxy-4-propylphenol. The hydrogenation of the double bond was very facile and selective, affording 100% yield of 2-methoxy-4-propylphenol in just 10 min (Fig. 8). In contrast to cresols and phenol, aromatic ring hydrogenation was not observed, which can be explained by the limited access of eugenol or 2-methoxy-4-propylphenol to active platinum sites due to their bulkiness. This is in line with guaiacol transformation where the yield of products having saturated aromatic ring was <2%. The hydrogenation of allyl group in eugenol can be attributed to pore-mouth catalysis (the allyl chain entering platinum at pore mouth where the aromatic ring cannot adsorb properly). Alternatively it can indicate that the three substituents of the aromatic ring prevent its adsorption on platinum crystallites which ultimately excludes the aromatic ring saturation.

**Table 5**
Maximum molecular dimension of studied phenolics as estimated by using Chemsketch (ACD Labs) software.

| Compound | $d_{max}$ (Å) |
|---|---|
| Phenol | 6.06 |
| o-Cresol | 6.10 |
| m-Cresol | 6.48 |
| p-Cresol | 6.94 |
| Guaiacol | 6.68 |
| Eugenol | 8.97 |

## 4. Conclusions

Beta-zeolites-supported platinum catalysts were found to be suitable for hydrogenation and deoxygenation of phenol. The catalysts yielded either cyclohexanol (Pt/Z-23) or cyclohexane (Pt/Z-20D) depending on their preparation. The mildly dealuminated catalyst allowed better accessibility of active sites and as a result fast conversion of phenol was achieved in comparison with the not-dealuminated catalysts. Cresols, methyl substituted phenols, were less reactive than phenol and also exhibited lower selectivity to the ultimate product of combined hydrogenation and deoxygenation. Methoxy group was shown to hinder both hydrogenation and deoxygenation.

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## References

[1] G. Gellerstedt, G. Henriksson, in: M. Belgacem, A. Gandini (Eds.), Monomers, Polymers and Composites from Renewable Resources, Elsevier, Amsterdam, 2008, pp. 201–224.
[2] L. Petrus, M. Noordermeer, Green Chemistry 8 (10) (2006) 861–867.
[3] A. Corma, S. Iborra, A. Velty, Chemical Reviews 107 (6) (2007) 2411–2502.
[4] P. Mäki-Arvela, B. Holmbom, T. Salmi, D. Murzin, Catalysis Reviews – Science and Engineering 49 (3) (2007) 197–340.
[5] P. Gallezot, Catalysis Today 121 (2007) 76–91.
[6] M.J. Climent, A. Corma, S. Iborra, Green Chemistry 13 (3) (2011) 520–540.
[7] D. Kubička, I. Kubičková, J. Čejka, Catalysis Reviews – Science and Engineering (2012), http://dx.doi.org/10.1080/01614940.2012.685811.
[8] X. Tong, Y. Ma, Y. Li, Applied Catalysis A: General 385 (1–2) (2010) 1–13.
[9] J. Zakzeski, P. Bruijnincx, A. Jongerius, B. Weckhuysen, Chemical Reviews 110 (6) (2010) 3552–3599.
[10] J. Horáček, D. Kubička, F. Homola, I. Kubičková, Catalysis Today 179 (2012) 191–198.
[11] P. Mäki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm, J. Mikkola, Industrial Crops and Products 32 (3) (2010) 175–201.
[12] G. Schaub, A. Vetter, Chemical Engineering and Technology 31 (2008) 721–729.
[13] S. Yaman, Energy Conversion and Management 45 (5) (2004) 651–671.
[14] A. Bridgwater, Biomass and Bioenergy (2011), http://dx.doi.org/10.1016/j.biombioe.2011.01.048.
[15] D. Bulushev, J. Ross, Catalysis Today 171 (1) (2011) 1–13.
[16] M.F. Demirbas, M.F. Balat M., Journal of Scientific and Industrial Research 66 (2007) 797–804.
[17] A. Gayubo, A. Aguayo, A. Atutxa, B. Valle, J. Bilbao, Journal of Chemical Technology and Biotechnology 80 (2005) 1244–1251.
[18] S.R. Katikaneni, J. Adjaye, N. Bakhshi, Energy and Fuels 9 (1995) 1065–1078.
[19] W.W. Zmierczak, J.D. Miller, US Patent Application Publication US (2008) 2008/0050792 A1.
[20] J.S. Shabtai, W.W. Zmierczak, E. Chornet, US Patent (1999) 5 959 167.
[21] O.I. Senol, E.-M. Ryymin, T.-R. Viljava, A.O.I. Krause, Journal of Molecular Catalysis A: Chemical 277 (2007) 107–112.
[22] E.-M. Ryymin, L. Maija, M.L. Honkela, T.-R. Viljava, A.O.I. Krause, Applied Catalysis A: General 389 (2010) 114–121.
[23] E. Furimsky, F.E. Massoth, Catalysis Today 52 (1999) 381–495.
[24] W. Baldauf, U. Balfanz, M. Rupp, Biomass and Bioenergy 7 (1994) 237–244.
[25] E. Laurent, B. Delmon, Industrial and Engineering Chemistry Research 32 (1993) 2516–2524.
[26] R.K.M.R. Kallury, W.M. Restivo, T.T. Tidwell, D.G.B. Boocock, A. Crimi, J. Douglas, Journal of Catalysis 96 (1985) 535–543.
[27] T. Nimmanwudipong, R.C. Runnebaum, D.E. Block, B.C. Gates, Energy and Fuels 25 (2011) 3417–3427.
[28] C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, Angewandte Chemie International Edition 48 (2009) 3987–3990.
[29] M.W. Deem, J.M. Newsam, Journal of the American Chemical Society 114 (1992) 7189–7198.
[30] C. Márquez-Alvarez, A.B. Pinar, R. García, M. Grande-Casas, J. Pérez-Pariente, Topics in Catalysis 52 (2009) 1281–1291.
[31] V. Tokarová, et al., submitted to Catalysis letters.
[32] C. Zhao, J. He, A.A. Lemonidou, X. Li, J.A. Lercher, Journal of Catalysis 280 (2011) 8–16.