



# Isomerization of dihydroxybenzenes over metal-zeolite catalysts through the carbonaceous deposits

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## ABSTRACT

Dihydroxybenzenes, including catechol, resorcinol and hydroquinone, have significant commercial value for a variety of applications such as adhesives, resins, pharmaceuticals, coatings etc. However, selective production of required isomers by phenol hydroxylation represents a considerable challenge.

Here, we report a new approach for the synthesis of dihydroxybenzenes by their isomerization using a bifunctional Pt/ZSM-5 catalyst. The catalyst successfully facilitates the transformation of catechol and hydroquinone to each other with a selectivity of up to 74 % and yields up to 50 %. The investigation of the mechanism suggests that isomerization proceeds via a carbonaceous deposit (coke) formed by intermediate quinone condensation with subsequent hydrogenolysis to isomers. The proposed mechanism shows the way for the design of the efficient process for isomerization of dihydroxybenzenes.

## 1. Introduction

Dihydroxybenzenes, also known as benzenediols, represent a class of aromatic compounds with two hydroxyl (–OH) groups attached to a benzene ring [1–3]. These molecules play a pivotal role in various fields, ranging from pharmaceuticals and agrochemicals to materials science and natural product synthesis [4]. For example, catechol (1,2-dihydroxybenzene) has been utilized in the development of bio-inspired adhesives, corrosion inhibitors and the synthesis of various pharmaceuticals and biologically active compounds [5,6]. Resorcinol (1,3-dihydroxybenzene) is used in the pharmaceutical industry in the synthesis of antiseptics and pharmaceutical drugs and it is a key component in the production of resins for the rubber industry [7]. Hydroquinone (1,4-dihydroxybenzene) is widely used in photography, cosmetics and as a polymerization inhibitor [8].

The global annual demand for dihydroxybenzenes is more than 200,000 metric tons [9,10]. Various dihydroxybenzenes can be produced by lignin depolymerization. However, the wide range of products obtained and the difficulties involved in separating them make this route less attractive [11]. The main industrial route for the synthesis of

catechol and hydroquinone is the hydroxylation of phenol by hydrogen peroxide catalyzed by acids or zeolite catalysts (Fig. 1). For example, Rhone-Poulence technology is based on the reaction of phenol with concentrated hydrogen peroxide or formic acid in the presence of phosphoric acid at 90 °C [12]. Metal-zeolite catalysts are also capable of oxidizing phenol with hydrogen peroxide to yield catechol and hydroquinone [13]. Ketone peroxides formed in-situ from ketone and hydrogen peroxide also have been used for hydroxylation of phenol in the presence of an acid catalyst [14]. Enichem technology is based on phenol oxidation over zeolite TS-1 [15–17]. The processes require high phenol/hydrogen peroxide ratios (about 20) at high concentrations of phenol (>30 %) to avoid overoxidation problems and provide selectivity to dihydroxybenzenes more than 90 % at hydrogen peroxide selectivity 60–90 % at the conversion of phenol less than 25 % [18]. Hydroquinone is typically produced in greater quantities than catechol, and the ratio depends on reaction conditions, such as temperature, concentrations of reactants, solvent and type of catalyst [19,20]. There are several issues related to the processes. First, relatively low selectivity due to overoxidation of phenol ring with formation of the mixture of acids and polymeric compounds. Another important issue is low control of

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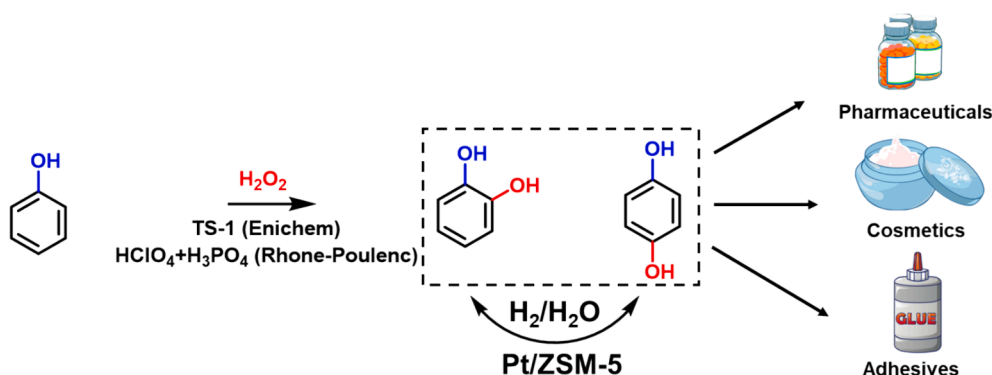


Fig. 1. State of the art and a proposed route for isomerization of dihydroxybenzenes.

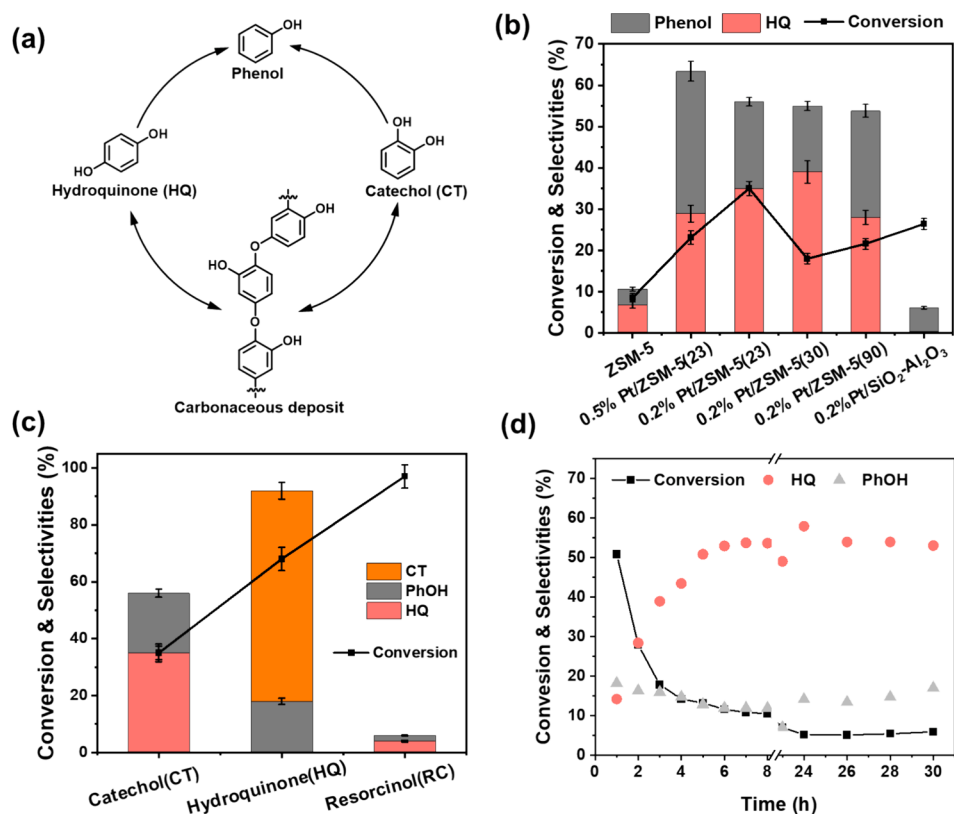


Fig. 2. (a) Scheme of the isomerization reaction; (b) The isomerization of catechol over different catalysts; (c) The isomerization of different dihydroxybenzenes over 0.2 % Pt/ZSM-5(30) and (d) The isomerization of catechol in time over 0.2 % Pt/ZSM-5(30). Conditions: 400 °C, 100 g/L dihydroxybenzene solution (water as solvent), 1.8 mL/h liquid flow rate, 30 mL/min H<sub>2</sub>, 1 bar, 0.15 g catalyst, TOS at 3 h.

regioselectivity during oxidation of phenol, which results in excessive production of hydroquinone in comparison with catechol. Thus, the abundance of isomers from the hydroxylation process does not match exactly those required for further use.

To solve these problems, it would be highly desirable to find a way of selective isomerization of the dihydroxybenzenes from one to another, which would solve the problem of selectivity and excessive production of one of the compounds (Fig. 1). At the moment, the main route for the conversion of dihydroxybenzenes is pyrolysis at 700–1000 °C for the production of C<sub>1</sub>–C<sub>6</sub> products [19]. The isomerization of alkylaromatics over acid catalysts is the major process in the industry [21–23]. For example, xylene isomerization in the narrow pores of zeolite ZSM-5 allows one to meet the high demand for *para*-xylene as the precursor of polyesters by converting the much less used *meta*- and *ortho*-xylenes [24]. Protonation of xylene results in the generation of carbonium ions

with the transfer of methyl group from one carbon atom of the ring to another [25].

Herein, we report an isomerization of dihydroxybenzenes over Pt/ZSM-5 catalyst at 400 °C using water as solvent in the presence of hydrogen. The optimized catalyst can provide selectivity in the isomerization of hydroquinone to catechol of 74 % and yield up to 50 %. The investigation of the mechanism of the reaction indicates the key role of intermediate carbonaceous deposits so-called coke in isomerization.

## 2. Results and discussion

### 2.1. Isomerization of dihydroxybenzenes

Isomerization of dihydroxybenzenes has been performed in a fixed bed reactor using H-ZSM-5 zeolite with and without Pt. The catechol,

hydroquinone or resorcinol have been dissolved in water and fed to the catalyst layer at 400 °C in the flow of hydrogen with subsequent analysis of the liquid products at the exit of the reactor. The main products of the reaction depending on the dihydroxybenzene being reacted are catechol and hydroquinone as the products of isomerization and phenol as the product of dehydroxylation (Fig. 2a, Fig. S1, SI). The activity of the catalyst is higher at the initial period with a decrease of the activity in time due to deactivation of the active sites (Fig. 2d, Fig. S2, SI). The analysis of the isomerization of catechol over 0.2 % Pt/ZSM-5(30) over time demonstrates a similar 15 % selectivity to phenol and hydroquinone during the initial period. The low selectivity to the products in the liquid phase arises from the significant formation of carbonaceous deposits over the catalyst's surface as a side product of the reaction, which prevents the selectivity in Fig. 2 from reaching 100 %. It also explains the deactivation of the catalyst due to the deposition of carbonaceous species. The activity decreases fast during the reaction reaching stable catalytic performance after about 20 h. The selectivity to hydroquinone increases in time reaching more than 50 % due to a decrease in the condensation rate of catechol to coke. Pure ZSM-5 has almost no isomerization activity of catechol (Fig. 2b). Amorphous aluminosilicate modified by Pt provides only traces of hydroquinone with phenol as the main product of the reaction indicating the key role of Pt in hydrogenolysis of catechol to phenol. The low acidity of amorphous aluminosilicate results in the low isomerization activity of the catalysts. Further, the work has been focused on the analysis of the metal and acidic functions on the catalytic performance of Pt/ZSM-5 in the reaction by variation of Pt quantity and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, respectively.

The XRD analysis of the catalysts demonstrates patterns corresponding to MFI structure and no peaks of Pt due to the low content and high dispersion of metal (Fig. S3, SI) [26]. There is also a similar surface area and pore volume of ZSM-5 catalysts with a small effect of Pt on the textural properties of the catalysts (Fig. S4, SI). The catalyst 0.2 %Pt/ZSM-5(30) after the reaction shows almost complete pore blockage, with a decrease in pore volume to a negligible 0.002 cm<sup>3</sup>/g compared to the initial volume of 0.15 cm<sup>3</sup>/g. The variation of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> from 23 to 90 leads to a proportional decrease in the number of acid sites and their strength measured by TPD of adsorbed NH<sub>3</sub> (Fig. S5, SI). The presence of Pt slightly decreases the amount of acid sites most probably due to the interaction of acid sites with Pt [27]. According to previous publications, the unusual effect of an increase in the strength of the acid sites with the amount of Al can be attributed to the generation of super acid extra-lattice aluminium species [28]. Analysis of the FTIR spectra of ZSM-5 (30) (Fig. S6, SI, Table S1, SI) demonstrates the presence of intensive bands observed at 3743 and 3608 cm<sup>-1</sup>, attributed to silanol groups and bridging hydroxyl groups (Si-(OH)-Al), respectively. The bands at 3783 and 3660 cm<sup>-1</sup> are usually assigned to the hydroxyl group attached to the tricoordinated Al atom partially connected to the framework and non-framework Al-OH, respectively [29]. The results show that pyridine interacts with all hydroxyl groups except silanols, with the appearance of bands at 1545 and 1455 cm<sup>-1</sup>, responsible for the interaction of Py with Brønsted acid sites and Lewis acid sites, respectively. The presence of Pt results in a decrease in the intensity of OH groups and the amounts of Brønsted and Lewis acid sites according to Py adsorption (Table S1, SI), confirming the interaction of Pt with acid sites.

TEM shows a uniform distribution of Pt in the crystal of ZSM-5 with particle sizes in the range from 0.5 to 5 nm with an average size of about 1.5 nm (Fig. S7, SI). STEM-HAADF analysis of the catalyst after the reaction also demonstrates an increase in the size of Pt nanoparticles to almost twice their original size, reaching about 3 nm, indicating the sintering process during the isomerization of dihydroxybenzenes (Fig. S8, SI). According to XPS Pt is in the reduced state after catalyst preparation with the peak of Pt 4f centered at a binding energy of 71.3–71.6 eV corresponding to metallic Pt (Fig. S9, SI) [30].

It should be noted that a decrease of Pt content from 0.5 to 0.2 wt% results in a significant increase of the selectivity to hydroquinone after 3 h of reaction from 29 to 39 % due to a decrease of the yield of phenol

(Fig. 2b). Thus, excess Pt mainly contributes to the dehydroxylation of catechol to phenol by hydrogenation over Pt sites. Pd-modified ZSM-5 demonstrates similar performance to the Pt-based catalyst (Fig. S10, SI). However, Ru and Ni exhibit lower activity and selectivity, most probably due to the lower dehydrogenation activity of these metals.

The decrease of acidity by an increase of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio from 23 to 90 results in a decrease of the conversion and selectivity to hydroquinone with an increase of the contribution of phenol. Thus, these results demonstrate the importance of the presence of low Pt content at high acidity of the catalyst for efficient isomerization of dihydroxybenzenes.

The isomerization ability of the 0.2 % Pt/ZSM-5(30) catalyst has been tested for other feeds (Fig. 2c). The feed of hydroquinone results in an increase in the conversion to 68 % with selectivity to catechol reaching 74 % at the yield of catechol about 50 %. The thermodynamic analysis [31] shows that catechol is more stable in comparison with hydroquinone, leading to an equilibrated ratio of catechol to hydroquinone of approximately 2 at 400 °C (Table S2, SI and Fig. S11, SI). Isomerization of catechol provides a ratio of catechol to hydroquinone of 5.4 and isomerization of hydroquinone provides a ratio of 1.6 in the products of the reaction, which is close to the thermodynamic equilibrium. It could be assigned to the smaller diameter of the hydroquinone molecule in comparison with catechol resulting in higher access to the acid and metal sites inside of the pores and higher isomerization activity. However, there is almost no isomerization of resorcinol to other products under the reaction conditions except generation of carbonaceous deposits over the catalyst resulting in a high conversion. There is also no resorcinol in the products of the reaction of isomerization of other dihydroxybenzenes. The protonation stabilizes ortho and *para*-carbocationic resonance forms, which should decrease accessibility for nucleophilic attack of *meta*-isomer for the synthesis of resorcinol [32]. Thus, it is similar to the isomerization of dialkylbenzenes such as xylene [33].

Deactivation is a serious problem for most high-temperature reactions such as MTO, Fischer-Tropsch, cracking, aromatisation, etc., including the isomerization of dihydroxybenzenes [34,35]. Usually, calcination in air is used for the regeneration of the catalyst with the removal of carbon species. Fig. S12, SI shows that calcination of the catalyst in the air results in regeneration with similar catalytic performance in time for the next cycles.

## 2.2. Mechanism of the reaction

Acid-catalyzed isomerization of dialkylaromatics such as xylene according to the literature proceeds by three possible routes depending on the catalyst and conditions: 1) intramolecular, 2) intermolecular by transalkylation and 3) dealkylation to olefin with subsequent realkylation [36].

The reaction of dihydroxybenzenes should proceed according to the hydrogen borrowing mechanism by intermediate dehydrogenation to quinones with subsequent protonation to carbocations and 1,2-migration of OH group, transfer to another molecule or dehydration to phenol and water with subsequent rehydration according to the mechanisms proposed earlier for isomerization of dialkylbenzenes.

Water could play a role in assisting dihydroxybenzene isomerization according to the last mechanism [37]. The isotope experiment has been conducted to understand the role of water during the isomerization. In the presence of isotope water (H<sub>2</sub>O<sup>18</sup>), the isomerization of catechol reaction over 0.2 % Pt/ZSM-5(30) catalyst at 400 °C and H<sub>2</sub> flow results in the synthesis of hydroquinone as the primary product without O<sup>18</sup> (Fig. S13, SI). However, the byproduct PhOH carries the O<sup>18</sup> label, which could be explained by the exchange of O of phenol with water. The oxygen exchange in phenol has been observed earlier in acidic media [38]. Also, it indicates that phenol cannot be an intermediate for the synthesis of hydroquinone.

The fact that dihydroxybenzenes undergo significant condensation on the catalyst surface with the generation of carbonaceous deposits

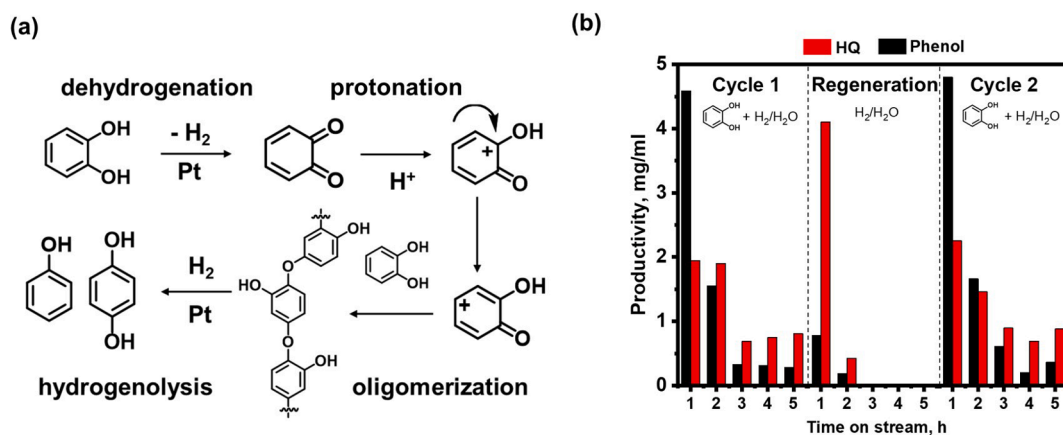


Fig. 3. Proposed mechanism of isomerization (a) and isomerization of catechol cycle followed by regeneration in H<sub>2</sub>/H<sub>2</sub>O flow over 0.2% Pt/ZSM-5(30) catalyst (b). Reaction conditions: 0.15 g catalyst, 100 g/L catechol aqueous solution, 1.8 mL/h liquid flow rate, 400 °C, 30 mL/min H<sub>2</sub>, 1 bar.

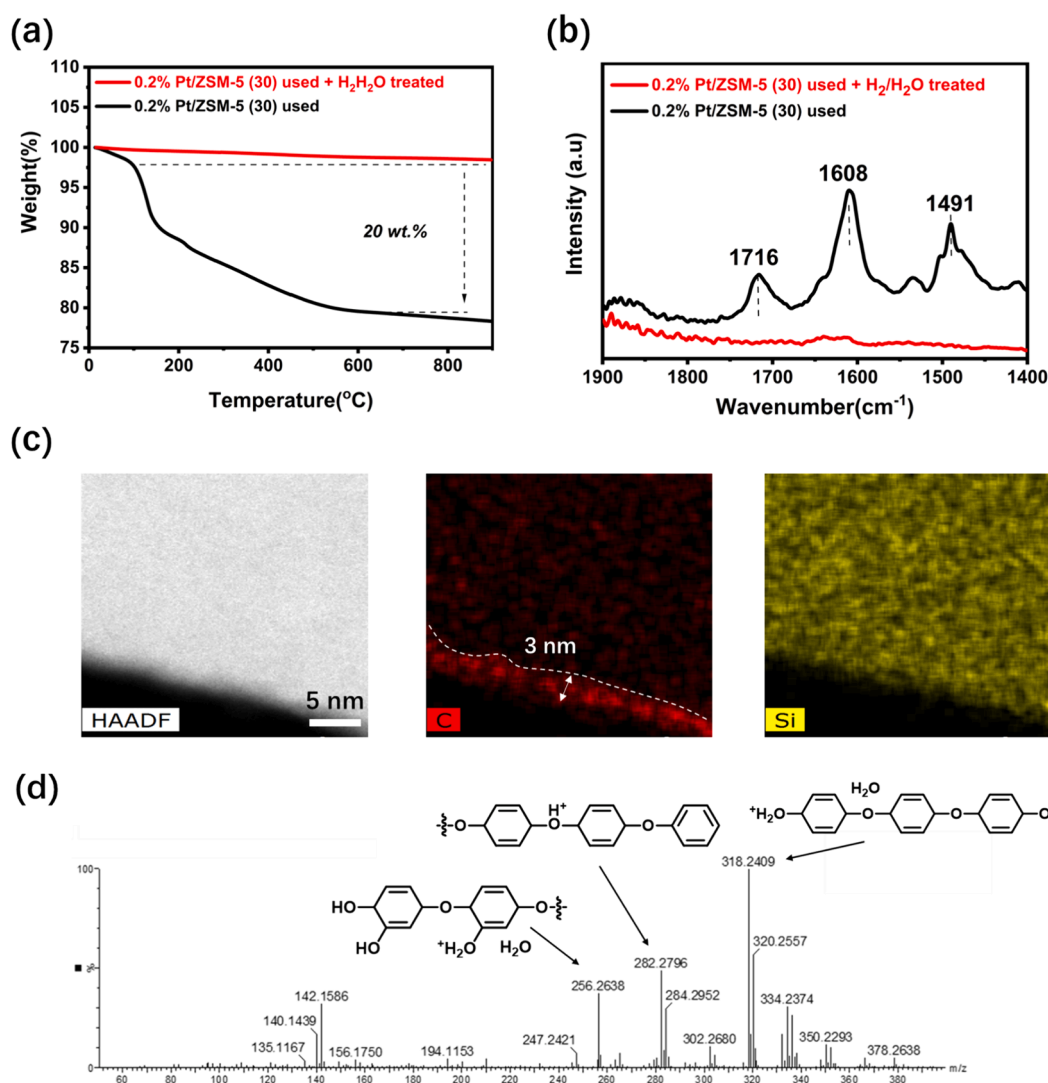


Fig. 4. The results of TG (a) and FTIR (b) analysis for the 0.2% Pt/ZSM-5(30) catalyst after reaction and after regeneration in H<sub>2</sub>/H<sub>2</sub>O, STEM-HAADF and EDX mapping of used catalyst (c) and LC-MS results for water solution after treatment of the used catalyst 0.2% Pt/ZSM-5(30) (d).

means that isomerization could proceed through an intermolecular mechanism with intermediate polymerization of dihydroxybenzenes and subsequent depolymerization with the generation of isomers. To

verify the assumption about polymeric species as an intermediate, we treated the washed deactivated catalyst in water vapours at 400 °C in hydrogen flow. Surprisingly, a significant amount of hydroquinone

additionally to the catechol has been detected in the liquid sample with the smaller contribution of phenol (Fig. 3). The formation of products stopped after 3 h of treatment. The catalyst after this treatment demonstrates the regeneration of the catalytic activity for the second cycle (Fig. 3).

The characterization of the used 0.2 % Pt/ZSM-5(30) catalyst by TG analysis (Fig. 4) confirms the presence of about 20 wt% of carbon species over the catalyst with decomposition and burning in the range of 200–600 °C. The FTIR peaks at 1716, 1608 and 1491  $\text{cm}^{-1}$  can be assigned to C=O, phenolic hydroxyl and aromatic ring vibrations, respectively [39]. Treatment in water vapours and hydrogen results in the disappearance of carbon deposits according to TGA and FTIR analysis indicating high reactivity of the formed polymer (Fig. 4). It can be proposed that the rate of accumulation of carbonaceous deposits during dihydroxybenzenes isomerization is higher than depolymerization at the initial step of the reaction, however, in time these rates are equilibrated with an increase of the selectivity to the isomerized products of the reaction.

The elemental mapping of TEM (Fig. 4 and Fig. S14, SI) clearly shows the presence of about 3 nm carbon layer localized mainly over the surface of 0.2 % Pt/ZSM-5(30) catalyst after the reaction. It seems the space limitations restrict polymer growth inside zeolite pores. The LC-MS has been used to identify the nature of the polymer species by treatment of the catalyst after reaction in water (Fig. 4). The species with molecular ions at 256, 282 and 318  $m/z$  have been detected in the products of extraction. They can be assigned to dimers and trimers containing different amounts of hydroxyl groups in the products. Thus, these polymer species could be intermediates during the isomerization of dihydroxybenzenes.

The potential mechanism of the isomerization reaction (Fig. 3a) can be described as the dehydrogenation of dihydroxybenzene to quinone over metal with subsequent protonation and oligomerization over the acid sites of ZSM-5 followed by hydrogenolysis over metal-acid sites to isomers. The Brønsted acid sites are expected to participate in these reactions by protonating quinones. However, it appears that even weak acid sites can be active, as aluminosilicates already produce some polymer (Fig. 2). Although dihydroxybenzenes are thermodynamically more stable compared to quinones (Table S2, SI), the reaction equilibrium should be shifted to the right due to the continuous consumption of formed quinones, leading to the generation of polymeric species. Subsequent hydrogenolysis of the polymer over metal-Brønsted acid sites results in the synthesis of isomers. This reaction is similar to the C-O bond cleavage during the depolymerization of lignin using zeolites promoted by metals [40]. The role of the proton in this case is in the protonation of O with subsequent hydride transfer to C and cleavage of the C-O bond.

Dihydroxybenzenes can readily penetrate the pores of zeolite. For instance, the diameter of hydroxyquinone is only 0.27 nm, whereas the pore size of ZSM-5 is 0.54 nm  $\times$  0.56 nm. Previous studies on reactions involving carbon deposition, such as MTO, have indicated internal condensation leading to the formation of low molecular weight internal coke. The diffusion of coke precursors outside the pores results in the formation of bulky external coke [39]. The nearly complete blockage of internal pores during the isomerization of dihydroxybenzenes indicates that external coke may participate in the reaction at high time on stream, involving external acid sites and Pt for coke formation and hydrogenolysis into isomers.

This mechanism is quite different from the traditionally proposed mechanisms for isomerization of dialkylbenzenes. Generation of carbocations from dihydroxybenzenes in comparison with dialkylbenzenes requires the presence of metal and acid sites for hydrogen borrowing mechanism to form quinones with subsequent protonation. Also, nucleophile O of dihydroxybenzenes is more reactive for nucleophilic attack with the formation of polymeric carbonaceous species. Dialkylbenzenes depending on zeolite and conditions participate in inter and intramolecular isomerization due to less reactive carbonium ions in

comparison with dihydroxybenzenes forming polymer compounds. Based on it we propose the isomerization of dihydroxybenzenes through intermediate synthesis of carbonaceous deposits and subsequent depolymerization to the isomers using metal-acid catalysts. Although the activities and selectivities proposed for this process are lower in comparison with those for the industrially used hydroxylation of phenol, this route does not consume expensive hydrogen peroxide and can be further optimized by variation of metal and acid functions. Also, this approach offers an opportunity to design the process based on polymerization-depolymerization sequences for more selective isomerization.

Traditionally coke is considered a negative aspect of catalysis resulting in periodic stops of the process of regeneration usually by the calcination of the catalyst in the air to burn out the carbon species [41]. The proposed process represents a unique situation when coke can be depolymerized to the products of the reaction. Earlier studies demonstrate only that coke could be a co-catalyst during reaction [42]. This strategy can be spread to other reactions where the reagents can form the polymeric species with subsequent depolymerization to the final products.

### 3. Conclusion

This study proposes a direct isomerization of dihydroxybenzenes to transform products from phenol hydroxylation (catechol and hydroquinone) to each other. Our catalytic results show successful reversible transformations of catechol and hydroquinone over the Pt/ZSM-5 catalyst. The reaction proceeds with the selectivity of up to 74 % and yields up to 50 %. The reaction proceeds by a hydrogen borrowing mechanism in a hydrogen atmosphere in water vapours at 400 °C with a decrease of the activity in time due to carbonaceous deposits formation, which forms by the dehydrogenation of dihydroxybenzenes into quinones with subsequent condensation over acid sites. These carbonaceous deposits can be converted to isomerized dihydroxybenzene by treatment in hydrogen and water flow confirming the role of these species in the reaction. This mechanism offers new insights into the isomerization process.

### CRedit authorship contribution statement

**Qiyang Wang:** Writing – original draft, Investigation, Data curation. **Mariya Shamzhy:** Data curation, Investigation. **Egon Heuson:** Investigation, Formal analysis. **Martine Trentesaux:** Investigation, Data curation. **Maya Marinova:** Investigation, Data curation. **Ahmed Addad:** Investigation, Data curation. **Fangzheng Su:** Resources, Investigation, Data curation, Conceptualization. **Vitaly V. Ordonsky:** Writing – review & editing, Supervision, Resources, Methodology, Data curation, Conceptualization.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

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