

## Article

# The ZSM-5-Catalyzed Oxidation of Benzene to Phenol with N<sub>2</sub>O: Effect of Lewis Acid Sites

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**Abstract:** The oxidation of benzene to phenol (BTOP) with N<sub>2</sub>O as the oxidant has been studied with a variety of Fe/ZSM-5 catalysts. The literature has conclusively proven that Fe<sup>2+</sup> sites are the active sites. However, some studies have suggested that the Lewis acidic sites (LAS) are responsible for the generation of the active chemisorbed oxygen. Nevertheless, there is no clear relationship between the LAS and the N<sub>2</sub>O selectivity to phenol. In an effort to elucidate the effects of LAS on BTOP with various ZSM-5 catalysts, we investigated the initial N<sub>2</sub>O selectivity to phenol. Here we show that the initial N<sub>2</sub>O selectivity to phenol is negative with the amount of LAS over a certain range. The catalyst H-ZSM-5-ST (H-ZSM-5 treated with water vapor) showed a remarkable initial N<sub>2</sub>O selectivity to phenol as high as 95.9% with a 0.021 mmol g<sup>−1</sup> LAS concentration on the surface of the catalyst, while the Fe/ZSM-5 catalyst demonstrated the lowest initial N<sub>2</sub>O selectivity to phenol (11.7%) with the highest LAS concentration (0.137 mmol g<sup>−1</sup>). Another remarkable feature is that steaming was more effective than Fe ion exchange and high temperature calcining. The samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), N<sub>2</sub>-adsorption-desorption, UV-vis, NH<sub>3</sub>-TPD and pyridine Fourier transform infrared (FT-IR) techniques. Our results demonstrate how the concentration of LAS is likely to affect the initial N<sub>2</sub>O selectivity to phenol within a certain range (0.021–0.137 mmol g<sup>−1</sup>). This research has demonstrated the synergy between the active Fe<sup>2+</sup> sites and LAS.

**Keywords:** N<sub>2</sub>O; ZSM-5; initial N<sub>2</sub>O selectivity to phenol; Lewis acidic sites; Brønsted acidic sites

## 1. Introduction

Phenol, which is an important organic chemical intermediate and raw material, is mainly used in the manufacture of phenolic resin, bisphenol A, and caprolactam. Nowadays, a commonly used industry process for developing phenol and acetone from benzene and propylene is the cumene process [1]. However, this process has the obvious disadvantage that phenol and acetone are used in a 1:1 ratio with the price of acetone heavily depending on the market demand. The market demand of acetone is smaller than that of phenol, which in terms of the market price of phenol is deeply influenced by that of the co-produced acetone. Thus, a more economical and environmentally friendly route is urgently needed. One route is suggested by the oxidation of benzene to phenol (BTOP) with nitrous oxide in one step as published by Iwamoto in 1983 [2]. In Iwamoto's research, V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> was used as the catalyst for the BTOP reaction. Later, a commonly used catalyst for the reaction is the H-ZSM-5 zeolites [3–5]. Recently, in order to improve on the activity of the H-ZSM-5 zeolites, Fe-ZSM-5 has been introduced. Iron for this catalyst can be supplied in various ways. Meloni et al. [6] discovered that in the total absence of Fe virtually no activity was observed. Igor et al. [7] studied Fe/ZSM-5 with a wide range of Fe content (0.015–2.1 wt.%) in the hydroxylation of benzene to phenol with nitrous oxide at low temperatures, and they found that both mono- and oligo-nuclear Fe(II) sites seem to be

responsible for the Fe/ZSM-5 activity in benzene hydroxylation. Further work was carried out by Krishnan et al. [8] as they differentiated three different types of Fe sites and concluded that benzene was oxidized into phenol with nitrous oxide over mononuclear Fe sites, while the reduction of  $\text{NO}_x$  to  $\text{N}_2$  with ammonia over binuclear Fe sites or the combustion of organic molecules to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  over hydrocarbons and Fe-oxide nanoparticles. Due to the superior properties of this catalyst, much research has focused on the role of Fe ion in BTOP reaction.

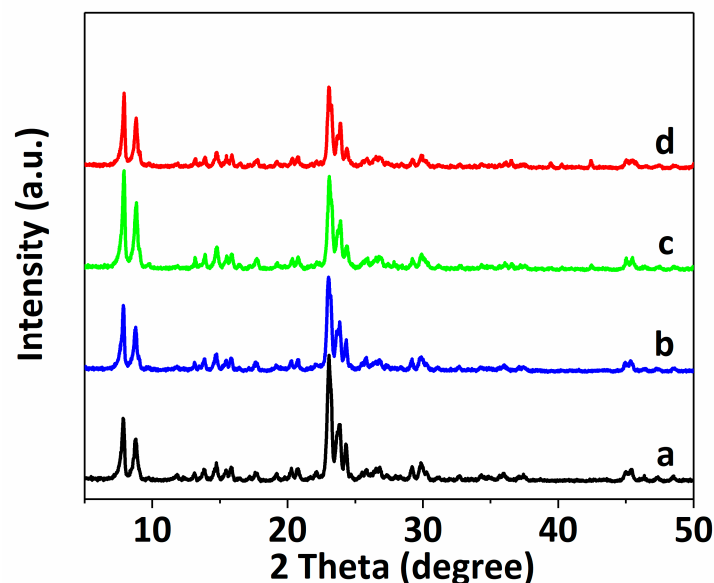
Pore size in the catalyst also plays a role in reactivity. The zeolite H-ZSM-5 has abundant micropores (0–2 nm), which strongly limit mass transfer of both the reactant benzene and the product phenol, the formation of coke leads to rapid catalyst deactivation [9–12]. In an attempt to achieve the improvement in the mass transfer limitations of the microporous zeolites catalysts, post-treatments such as steam and acid treatment for dealumination have been applied to generate mesopores (2–50 nm) in zeolites [9,13–15]. For example, Xin et al. [16] reported synthesis of a highly active hierarchical Fe/ZSM-5 zeolite catalyst that strongly enhances the lifetime in benzene hydroxylation to phenol. In another approach, Koekkoek et al. [9] utilized a di-quaternary ammonium surfactant to synthesize hierarchical Fe/ZSM-5 zeolites consisting of thin sheets limited in growth in the b-direction which improved catalytic performance.

Because most of the attention was focused on the roles of Fe ions and mesopores, there was little research on exploring the changes of acidity induced by post treatment. For example, Jia et al. [8] proposed that steam treated Fe/ZSM-5 (Fe/ZSM-5-ST) was used as catalyst, and Lewis acidic sites (LAS) were the active sites, without studying the detailed differences of acidity before and after steam treatment. To resolve this question, we carried out a systematic exploration about the amount, the type and the intensity of acid before and after steam treatment. Currently, steam treatment is used to improve the performance of the H-ZSM-5 catalyst for the hydroxylation of benzene to phenol, resulting in enhanced activity and stability for the hydroxylation reaction. Steam treatment leads to great changes in the amount, the type, and the intensity of acid. Therefore, in this study we estimated the physicochemical properties of catalysts by means of X-ray diffraction (XRD), scanning electron microscope (SEM),  $\text{N}_2$  adsorption-desorption and UV-vis. Temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) and pyridine Fourier transform infrared (FT-IR) spectra were applied to study the properties of acid. Finally, the performance of the Fe/ZSM-5-ST catalyst in the benzene hydroxylation to phenol reaction was investigated.

## 2. Results and Discussion

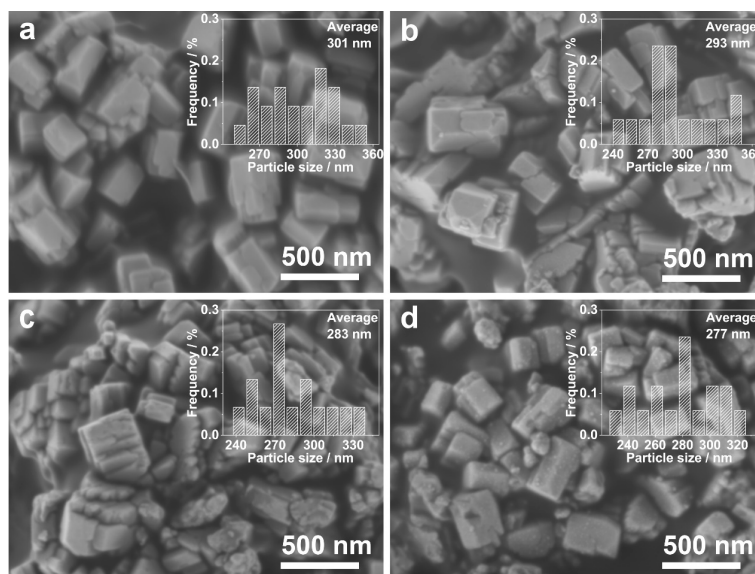
### 2.1. Physicochemical Properties of Catalysts

The wide-angle XRD patterns (Figure 1 and Figure S1) show that the intrinsic lattice structure of the MFI topology is observed in all the samples, and there is no  $\alpha\text{-Fe}_2\text{O}_3$  diffraction peak (reflections at  $2\theta = 33.2^\circ$  and  $35.7^\circ$ ) [17] nor any other iron oxides observed because the amount of Fe is too low [18]. However, the intensity of the Fe/ZSM-5 decreased with the addition of Fe due to the higher X-ray absorption coefficient of Fe compounds [19]. And the samples with high temperature water vapor steaming treatment showed a lower intensity due to the removal of Al from the zeolite framework [20].



**Figure 1.** X-ray diffraction (XRD) patterns of (a) H-ZSM-5, (b) Fe/ZSM-5, (c) H-ZSM-5-ST and (d) Fe/ZSM-5-ST.

The representative SEM images in Figure 2 show that the crystal size (ca. 300 nm) of H-ZSM-5 changed slightly after controlled ion exchange of  $\text{Fe}(\text{NO}_3)_3$ , while smaller size particles occur around the zeolite after steam treatment.



**Figure 2.** Scanning electron (SEM) images of (a) H-ZSM-5, (b) Fe/ZSM-5, (c) H-ZSM-5-ST and (d) Fe/ZSM-5-ST.

$\text{N}_2$  adsorption and desorption isotherms of the conventional H-ZSM-5, Fe/ZSM-5, H-ZSM-5-ST and Fe/ZSM-5-ST samples are presented in Figure 3A. The comparative curves of the pore-size distribution, which are calculated from adsorption isotherms using the density functional theory (DFT) model, are shown in Figure 3B. BET surface area and total pore volume are given in Table 1. As shown in Figure 3A, all the four samples exhibit isotherms with mixed types, Type I and Type IV, according to the International Union of Pure and Applied Chemistry (IUPAC) classification. Predominant adsorption ended below  $P/P_0 = 0.02$  (due to micropore filling or capillary condensation) and a hysteresis loop extended from  $P/P_0 = 0.4$  to  $\sim 1$  (associated with the presence of large mesopores

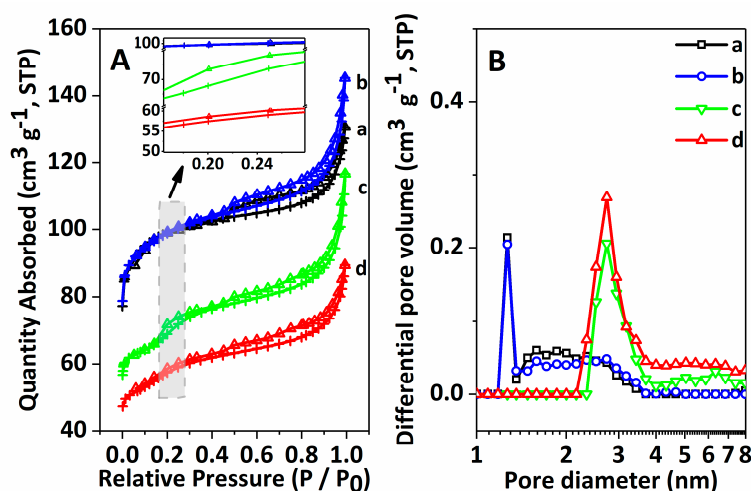
arising from textural mesoporosities) as present in all samples, there are other unique features in the isotherms of H-ZSM-5-ST and Fe/ZSM-5-ST samples. One of these features is a pore filling step at  $P/P_0 \sim 0.2$ , which is not observed for ZSM-5 without water vapor treatment, ascribable to pore filling into supermicropores or small mesopores [21,22]. Furthermore, the pore size distribution curves presented in Figure 3B show mesopores over a narrow distribution of mesopore diameter centered at 2.7 nm. Both Fe/ZSM-5 and H-ZSM-5 samples show sharp uptakes in the adsorption capacity at low pressures and end at almost the same adsorption levels, suggesting that the two samples have similar amounts of micropores with the same supermicropore diameter with a median of 1.3 nm. This illustrates that the controlled ion exchange does not affect the crystallinity, and thus the intrinsic micropores were well preserved [23]. Both the H-ZSM-5-ST sample and the Fe/ZSM-5-ST sample have a decrease in the number of the micropores, especially the latter one, indicating changes caused by water steam treatment [22,24].

**Table 1.** The pore distribution properties of H-ZSM-5, Fe/ZSM-5, H-ZSM-5-ST and Fe/ZSM-5-ST.

| Samples     | Surface Area ( $\text{m}^2 \text{g}^{-1}$ ) |                     |                      | $S_{\text{meso}}^b/S_{\text{micro}}^c$ | Pore Volume ( $\text{cm}^3 \text{g}^{-1}$ ) |                     |                      | $V_{\text{meso}}^e/V_{\text{micro}}^f$ |
|-------------|---------------------------------------------|---------------------|----------------------|----------------------------------------|---------------------------------------------|---------------------|----------------------|----------------------------------------|
|             | $S_{\text{BET}}^a$                          | $S_{\text{meso}}^b$ | $S_{\text{micro}}^c$ |                                        | $V_{\text{tot}}^d$                          | $V_{\text{meso}}^e$ | $V_{\text{micro}}^f$ |                                        |
| H-ZSM-5     | 337                                         | 87                  | 250                  | 0.35                                   | 0.24                                        | 0.14                | 0.11                 | 1.27                                   |
| Fe/ZSM-5    | 336                                         | 92                  | 244                  | 0.38                                   | 0.24                                        | 0.14                | 0.11                 | 1.27                                   |
| H-ZSM-5-ST  | 240                                         | 116                 | 124                  | 0.93                                   | 0.26                                        | 0.17                | 0.09                 | 1.89                                   |
| Fe/ZSM-5-ST | 196                                         | 92                  | 104                  | 0.88                                   | 0.28                                        | 0.18                | 0.10                 | 1.80                                   |

<sup>a</sup> BET surface area; <sup>b</sup>  $S_{\text{meso}}$  =  $S_{\text{BET}} - S_{\text{micro}}$ ; <sup>c</sup> t-plot micropore surface area; <sup>d</sup> Pore volume at  $P/P_0 = 0.99$ ;

<sup>e</sup>  $V_{\text{meso}}$  =  $V_{\text{tot}} - V_{\text{micro}}$ ; <sup>f</sup> t-plot micropore volume.



**Figure 3.** (A)  $\text{N}_2$  adsorption/desorption isotherms and (B) the corresponding pore-size distribution as derived from  $\text{N}_2$  sorption (DFT on the adsorption branch) of (a) H-ZSM-5, (b) Fe/ZSM-5, (c) H-ZSM-ST and (d) Fe/ZSM-5-ST.

The decreased BET surface areas and pore volume is presented in Table 1. H-ZSM-5 and Fe/ZSM-5 have very similar BET surface areas, 337 and 336  $\text{m}^2 \text{g}^{-1}$ , respectively. For H-ZSM-5-ST, the mesoporous surface area is 109  $\text{m}^2 \text{g}^{-1}$ , and the mesoporous volume is 0.12  $\text{cm}^3 \text{g}^{-1}$ , while the values for Fe/ZSM-5-ST are 93  $\text{m}^2 \text{g}^{-1}$  and 0.09  $\text{cm}^3 \text{g}^{-1}$ , respectively. However, the gain in mesoporosity and the value of  $S_{\text{meso}}^b/S_{\text{micro}}^c$  and  $V_{\text{meso}}^e/V_{\text{meso}}^f$  is accompanied by a loss of microporosity. As the microporous areas of H-ZSM-5 and Fe/ZSM-5 are 250 and 244  $\text{m}^2 \text{g}^{-1}$ , the microporous surface areas decreased to 124 and 104  $\text{m}^2 \text{g}^{-1}$  for H-ZSM-5-ST and Fe/ZSM-5-ST after water vapor treatment. The microporous volume also decreases with the generation of mesopores, with changes of the pore structure. It is obvious that the value of  $V_{\text{meso}}^e/V_{\text{meso}}^f$  has a prominent increase, from 1.27 to  $\sim 1.80$ . H-ZSM-5-ST and Fe/ZSM-5-ST demonstrate a loss of micropore volume with an increase of mesopore

volume. As it is known that catalysts with higher mesoporosity are likely to have longer endurance in the catalytic reactions, the mesopores can offer not only reaction interface, but also a diffusion path for mass transfer [9,16,25]. A suitable match between the micropores and mesopores is probably one of the factors that benefit the reaction.

As shown in Figure 4, the Fe/ZSM-5 sample exhibits one dominant absorption band at 249 nm with some poorly resolved bands at 228, 325, 480, and 545 nm, while Fe/ZSM-5-ST predominantly features two bands at 249 and 325 nm, respectively. According to the results from the literature [26–29], the bands at 228 and 249 nm are assigned to the oxygen-to-iron charge transfer transition of isolated  $\text{Fe}^{3+}$  in tetrahedral coordination in the framework. Octahedral ferric species in small oligonuclear clusters are characterized by absorptions around 325 nm [30]. The shoulder centered at 480 nm is associated with  $\text{Fe}_2\text{O}_3$  nanoparticles at the external surface of the zeolite crystal, while the shoulder centered at 545 nm is ascribed to bulk forms of iron oxide [9,26]. With Fe/ZSM-5, the intensities of bands, one of which is between 300 and 400 nm, and another one of which is above 400 nm are much lower for Fe/ZSM-5-ST. It can be concluded that the increase of isolated Fe ions in tetrahedral, higher coordination and oligomeric  $\text{Fe(III)}_x\text{O}_y$  clusters is due to the decrease of the aggregates  $\text{Fe}_2\text{O}_3$  nanoparticles (see Table 2) after steam treatment.

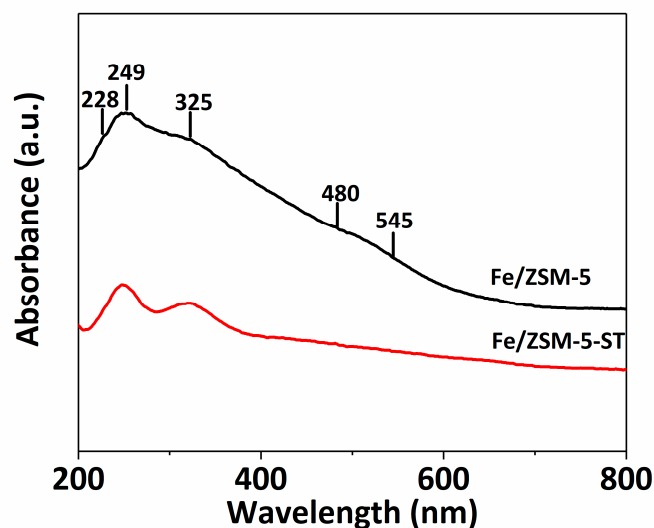


Figure 4. UV-vis spectra of Fe/ZSM-5 and Fe/ZSM-5-ST.

**Table 2.** Percentage of the area of the bands ( $A_1$  at  $\lambda < 300$  nm,  $A_2$  at  $300 < \lambda < 400$  nm and  $A_3$  at  $\lambda > 400$  nm) estimated by deconvolution of the UV-vis spectra of the catalysts.

| Samples     | $A_1$ <sup>a</sup> [%] | $A_2$ <sup>b</sup> [%] | $A_3$ <sup>c</sup> [%] |
|-------------|------------------------|------------------------|------------------------|
| Fe/ZSM-5    | 20                     | 52                     | 28                     |
| Fe/ZSM-5-ST | 35                     | 54                     | 11                     |

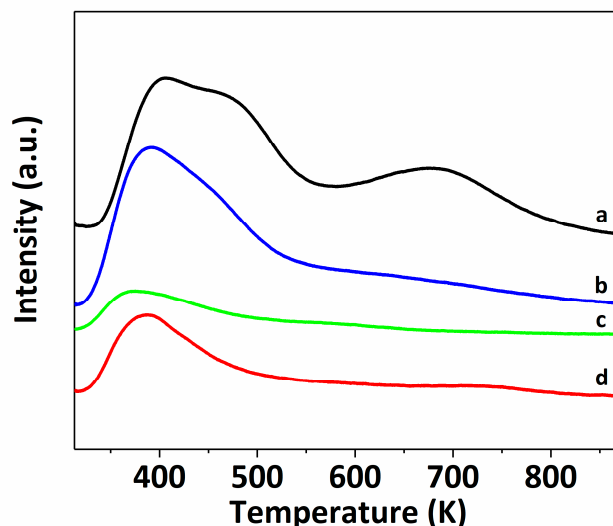
<sup>a</sup> Isolated  $\text{Fe(III)}$  ions in tetrahedral and higher coordination; <sup>b</sup> Oligomeric  $\text{Fe(III)}_x\text{O}_y$  clusters;

<sup>c</sup> Aggregated  $\text{Fe}_2\text{O}_3$  particles.

## 2.2. Catalysts Acidity

To evaluate the change in the acidic properties of different materials, the acidity of the studied samples was estimated on the groups of TPD of ammonia and pyridine-FTIR. As presented in Figure 5, the  $\text{NH}_3$ -desorption profile exhibits a broad band at the range of 313–873 K. H-ZSM-5 exhibits two desorption peaks at about 400 and 683 K, corresponding to the weak acidic sites and strong acidic sites, respectively [31]. With the ion exchange of  $\text{Fe(NO}_3)_3$ , the low-temperature peak migrates to lower temperature, suggesting that the acid strength become weaker probably because of the weaker acidity of  $\text{Fe-OH-Si}$  [32], and the amount weak acidic sites for Fe/ZSM-5 decrease with ferric species

incorporation into the ZSM-5 framework [33]. Both H-ZSM-5-ST and Fe/ZSM-5-ST samples show much less acid amounts than samples without water steam treatment in Table 3, due to the serious dealumination of zeolite framework [34]. As we can also see that H-ZSM-5 exhibits a shoulder centered at 475 K has been attributed to  $\text{NH}_3$  weakly adsorbed on Brønsted acid sites [35]. The intensity of the peak at 473 K for Fe-ZSM-5 sample also decreases with Fe loading, supporting the attribution of this peak to weak Brønsted acid sites [36]. Thus, the shoulder belongs to the weak acid sites, too. Moreover, the amount of strong acidic sites related to H-ZSM-5-ST is  $0.25 \text{ mmol g}_{\text{catal}}^{-1}$ , which is much lower than  $1.13 \text{ mmol g}_{\text{catal}}^{-1}$  belonging to H-ZSM-5. And the amount of strong acidic sites related to Fe/ZSM-5-ST is  $0.37 \text{ mmol g}_{\text{catal}}^{-1}$ , which is much lower than  $1.05 \text{ mmol g}_{\text{catal}}^{-1}$  attributing to Fe/ZSM-5. Furthermore, the quantity of weak acidic sites of H-ZSM-5-ST is  $0.24 \text{ mmol g}_{\text{catal}}^{-1}$ , which is almost six times lower than  $1.70 \text{ mmol g}_{\text{catal}}^{-1}$  of H-ZSM-5-ST, and the quantity of weak acidic sites of Fe/ZSM-5-ST is  $0.52 \text{ mmol g}_{\text{catal}}^{-1}$ , which is obviously 1 time less than  $1.33 \text{ mmol g}_{\text{catal}}^{-1}$  of Fe/ZSM-5-ST. From Table 3, it can be concluded that the order of total amount of acidic sites is: H-ZSM-5 > Fe/ZSM-5 > Fe/ZSM-5-ST > H-ZSM-5-ST. Although the total acidic sites reduce because of water vapor treatment, the total quantity of Fe/ZSM-5-ST owns a higher value compared to H-ZSM-5-ST. This is attributed to the existence of Fe species, which enhances the stability of acidic sites during the water vapor treatment [37,38].



**Figure 5.**  $\text{NH}_3$ -TPD spectra of the catalysts: (a) H-ZSM-5, (b) Fe/ZSM-5, (c) H-ZSM-5-ST and (d) Fe/ZSM-5-ST.

**Table 3.** Acidity of H-ZSM-5, Fe/ZSM-5, H-ZSM-5-ST and Fe/ZSM-5-ST estimated on the groups of  $\text{NH}_3$ -TPD profiles and from activity for reaction.

| Samples     | Total Acidity<br>( $\text{mmol g}_{\text{catal}}^{-1}$ ) | Weak Acidity<br>( $\text{mmol g}_{\text{catal}}^{-1}$ ) | Strong Acidity<br>( $\text{mmol g}_{\text{catal}}^{-1}$ ) |
|-------------|----------------------------------------------------------|---------------------------------------------------------|-----------------------------------------------------------|
| H-ZSM-5     | 2.83                                                     | 1.70                                                    | 1.13                                                      |
| Fe/ZSM-5    | 2.38                                                     | 1.33                                                    | 1.05                                                      |
| H-ZSM-5-ST  | 0.49                                                     | 0.24                                                    | 0.25                                                      |
| Fe/ZSM-5-ST | 0.89                                                     | 0.52                                                    | 0.37                                                      |

The acid property is further tested by pyridine adsorbed FTIR spectra in Figure 6 (The acid property of calcined samples is presented in Figure S2 and Table S1). The spectra recorded after outgassing at 423 K and 573 K represent the total and strong acidic sites, respectively [39]. The  $1540 \text{ cm}^{-1}$  band is assigned to the vibration of pyridine molecules chemisorbed on Brønsted acidic sites (BAS), while the bands centered around  $1450 \text{ cm}^{-1}$  is correspond to the Lewis acidic sites (LAS). The  $1490 \text{ cm}^{-1}$  band contributed to the pyridine molecules chemisorbed on both Brønsted and

Lewis acidic sites. The intensities of the band centered at  $1540\text{ cm}^{-1}$  decrease after Fe ions-exchanged, which is opposite to that of the band centered at  $1450\text{ cm}^{-1}$  [24,40]. Moreover, it descends sharply after water vapor treatment. Furthermore, the lower peak presented at 573 K illuminates that high temperature steamed catalyst persists certain acidic sites of which the intensity is rather low. This result is in accordance with the results from  $\text{NH}_3$ -TPD. And the lower peak according to  $1540\text{ cm}^{-1}$  compared to  $1450\text{ cm}^{-1}$  elucidates that BAS loses more acidic sites when compared to LAS. The number of acidic sites for each sample, obtained from the corresponding integrated area of the absorbance peaks at 1540 and  $1450\text{ cm}^{-1}$ , are given in Table 4. The BAS amount of Fe/ZSM-5 is less than that of H-ZSM-5, especially, the total Brønsted acid amount, which is obtained through pyridine desorption at 423 K is  $0.22\text{ mmol g}^{-1}$ , one folder lower than  $0.46\text{ mmol g}^{-1}$ , whereas the total Lewis acidity is  $0.14\text{ mmol g}^{-1}$ , much higher than  $0.05\text{ mmol g}^{-1}$ . As a consequence, the ratio value of B/L (BAS/LAS) according to Fe/ZSM-5 is 1.57, which is five times lower than 9.20 owing to H-ZSM-5. As a result, the changes related to the acidic sites properties and intensities is due to the Fe species, which monitors the ratio of B/L, because some ferric species interact with the oxygen of the bridging hydroxyl groups by replacing the protons (ion-exchange effect) [37]. One is noteworthy is that when experiencing water vapor treatment, H-ZSM-5-ST and Fe/ZSM-5-ST lose almost all their initial BAS (tetrahedral-coordinated aluminum) due to the serious removal of framework aluminum of zeolite [33,41,42], hence, the prepared H-ZSM-5-ST and Fe/ZSM-5-ST own precious few BAS and certain amount of LAS with its acid strength decreasing, coinciding with the results from Jia et al. [8]. In addition, the agglomeration of the extra-framework Al to clusters exposing lower Lewis acidity after after steaming [43]. Clearly, visible is that the weak effect on LAS and the strong effect on BAS result in the reduction of B/L with a certain treatment, thus the steaming can regulate and control the value of B/L. These results clearly indicate that Fe ions-exchanged and high temperature steam treatment result in the changes of acidity including the amount, the intensity, and the ratio of B/L, moreover, the effect of steaming is more obvious. Based on the fact that benzene hydroxylation over ZSM-5 zeolite catalysts is a typical solid-acid catalytic reaction, and the microscopic acidic properties play a crucial role for its catalytic performance [42,43].

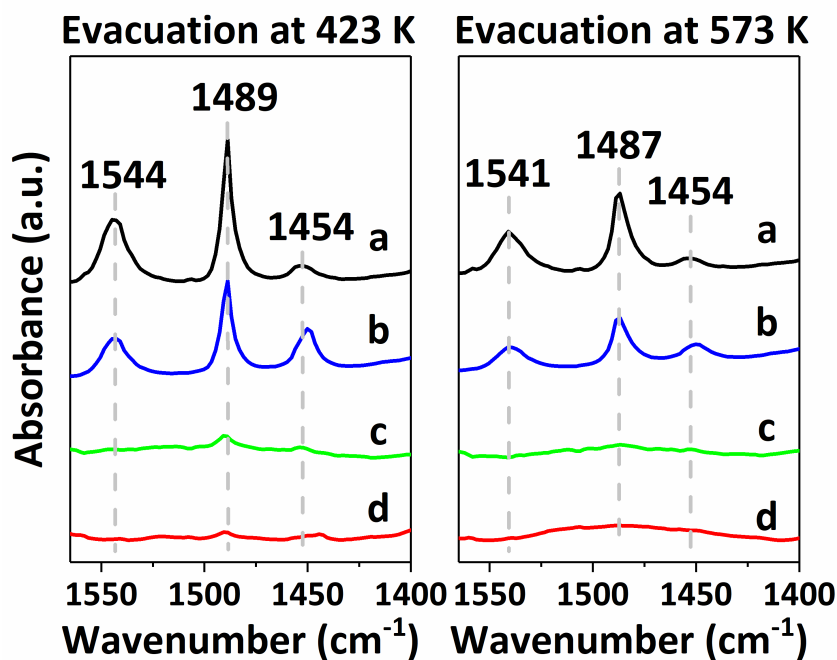


Figure 6. Pyridine FTIR spectra on (a) H-ZSM-5, (b) Fe/ZSM-5, (c) H-ZSM-5-ST and (d) Fe/ZSM-5-ST.

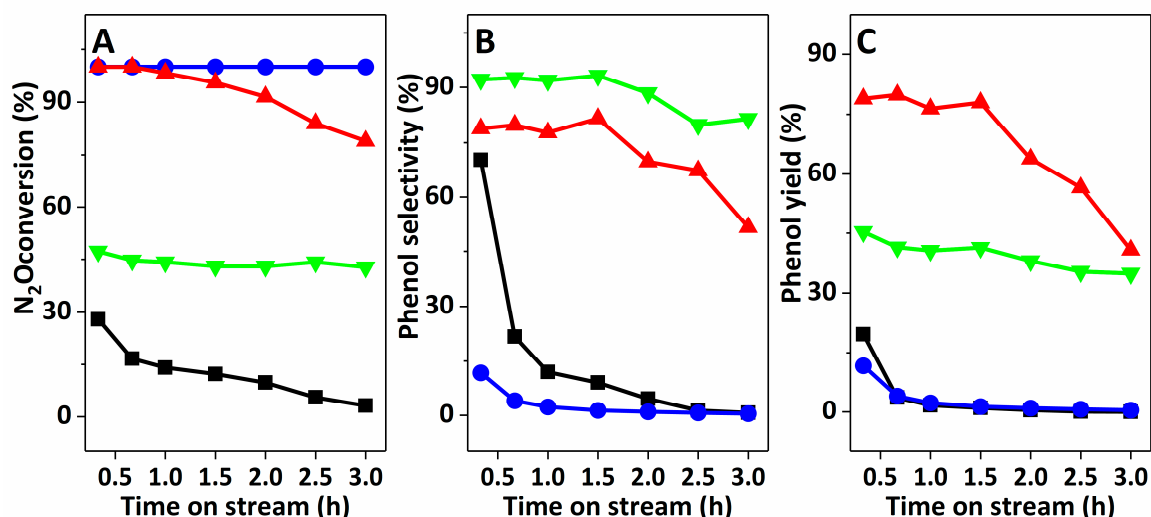
**Table 4.** Acidity properties from the Py-FTIR analysis for catalysts H-ZSM-5, Fe/ZSM-5, H-ZSM-5-ST and Fe/ZSM-5-ST.

| Samples     | 423 K (Total) (mmol g <sup>−1</sup> ) |                    | B/L  | 573 K (Strong) (mmol g <sup>−1</sup> ) |       | B/L  |
|-------------|---------------------------------------|--------------------|------|----------------------------------------|-------|------|
|             | Brønsted <sup>a</sup>                 | Lewis <sup>a</sup> |      | Brønsted                               | Lewis |      |
| H-ZSM-5     | 0.46                                  | 0.05               | 9.20 | 0.16                                   | 0     | –    |
| Fe/ZSM-5    | 0.22                                  | 0.14               | 1.57 | 0.09                                   | 0.02  | 4.50 |
| H-ZSM-5-ST  | 0.04                                  | 0.02               | 2.00 | 0                                      | 0     | –    |
| Fe/ZSM-5-ST | 0.02                                  | 0.03               | 0.67 | 0                                      | 0     | –    |

<sup>a</sup> Determined by FTIR spectra of absorbed pyridine.

### 2.3. Catalyst Performance in Benzene Hydroxylation Reaction

The catalytic performances of phenol yield over all four samples were evaluated on a continuous flow fixed-bed stainless tube reactor at 698 K and the indexes are detailed in Figure 7. The N<sub>2</sub>O conversion, phenol selectivity and yield evolution, which is regarded as a function of reaction time show all the four samples' performance during benzene hydroxylation to phenol reaction.



**Figure 7.** Effect of time on stream on (A) N<sub>2</sub>O conversion, (B) phenol selectivity and (C) yield over (a) H-ZSM-5 (■), (b) Fe/ZSM-5 (●), (c) H-ZSM-5-ST (▼) and (d) Fe/ZSM-5-ST (▲) catalysts. Reaction conditions: 698 K, 101 kPa, C<sub>6</sub>H<sub>6</sub>: N<sub>2</sub>O: He (molar ratio) = 10: 1: 9, a total weight hourly space velocity (WHSV) of 4320 mL g<sub>catal</sub><sup>−1</sup> h<sup>−1</sup>.

Figure 7A presents the conversion of N<sub>2</sub>O with time on stream. It can be clearly seen that the N<sub>2</sub>O conversion follows the order Fe/ZSM-5 > Fe/ZSM-5-ST > H-ZSM-5-ST > H-ZSM-5. Fe/ZSM-5 catalyst showed a full N<sub>2</sub>O conversion (100.0%) from the beginning to steady stage. On the other hand, Fe/ZSM-5-ST catalyst keeps a value of 100.0% at the initial time, and it falls rapidly down to 78.8% with time on steam (TOS). H-ZSM-5-ST also has a N<sub>2</sub>O conversion with its value stays around 47.2% at the initial time, and it goes down gradually to 42.7%. Additionally, H-ZSM-5 has a different discipline, with a N<sub>2</sub>O conversion declining from 28.0% to around 3.0%, thus, it can be speculated that the N<sub>2</sub>O conversion can be improved using different methods including ion-exchange and high temperature. Moreover, the N<sub>2</sub>O conversion reflects a tight relationship with the ferric species.

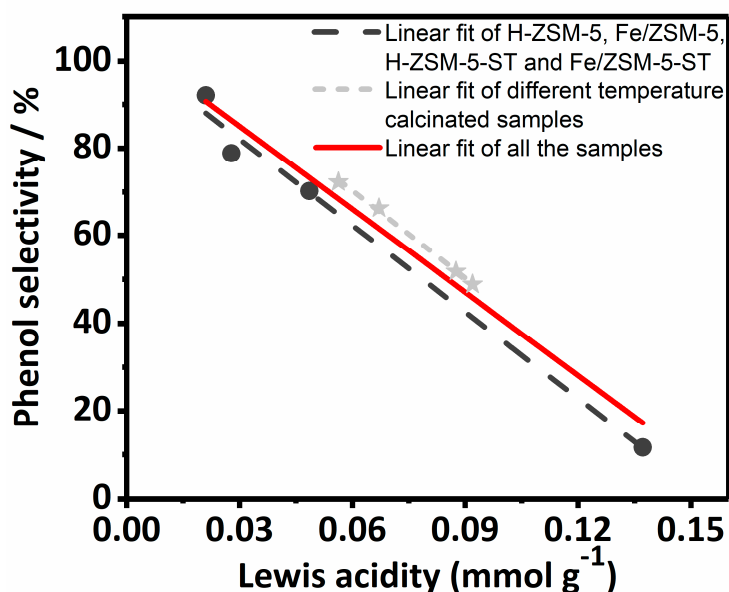
As Figure 7B shows, at the beginning period, the initial selectivity to phenol amounts boost to 70.2%, 95.9%, and 78.8% for the H-ZSM-5, H-ZSM-5-ST and Fe/ZSM-5-ST samples, respectively, much higher than that of Fe/ZSM-5 (11.7%) with an order of H-ZSM-5-ST > Fe/ZSM-5-ST > H-ZSM-5 > Fe/ZSM-5. Notably, a sharp drop from 70.2% to 0.1% is observed over H-ZSM-5 with reaction

proceeding. Conversely, H-ZSM-5-ST and Fe/ZSM-5-ST exhibit similar time-on-steam behavior, in which the stability and phenol selectivity are higher than H-ZSM-5 and Fe-ZSM-5, respectively. However, both selectivity declines rapidly after 90 min.

Figure 7C gives the yield toward phenol in all cases. Firstly, the yield of H-ZSM-5 and Fe/ZSM-5 are predominantly low with the significantly short lifespan. It is generally accepted that deactivation of zeolite catalysts in the benzene hydroxylation to phenol reaction mainly originates from coking [8,16,44,45]. Accordingly, the deactivation of oxidation of benzene to phenol is attributed to the coke deposits [9,45,46]. Combined the N<sub>2</sub> sorption experiments, it is noteworthy that H-ZSM-5-ST and Fe/ZSM-5-ST contain close mesopore volume and the ratio value of  $V_{\text{meso}}/V_{\text{micro}}$ , which are higher than those of H-ZSM-5 and Fe/ZSM-5, resulting in the longer lifetime. Moreover, Fe/ZSM-5-ST gain a high phenol yield around 80%. And H-ZSM-5-ST seems to have a higher yield than that of Fe-ZSM-5-ST after 3 h reaction time. Probably because catalysts containing Fe deactivated more severely and rapidly [47]. In addition, it is seen that the initial selectivity toward phenol has a certain relationship with the acid properties when combines the data from Figure 6, Figure 7, and Table 4. It may be safe to assume that precious few acidic sites, especially LAS, have a better effect on the initial selectivity toward phenol, which is consistent with that H-ZSM-5-ST and Fe/ZSM-5-ST owning lower acidic sites. Hence, according to the H-ZSM-5-ST and Fe/ZSM-5-ST catalysts with fewer acidic sites, the water vapor treatment is more beneficial not only for improving the initial selectivity but also for the enhanced catalytic lifespan. Furthermore, it is deduced that this observation supports acidity (low B/L ratio, low LAS amounts without strong BAS and LAS) adjusting by high temperature steaming that enhances the initial selectivity to phenol, and prolongs the lifetime, and reduce the side reactions at the same time [48]. In all cases, the ratio of B/L = 0.67 ascribed to Fe/ZSM-5-ST displays the best catalytic performance.

Comprehensively, on the basis of the N<sub>2</sub>O conversion and phenol selectivity analysis, and aforementioned acidity investigations, we, therefore, propose that the controlled ion-exchange and water vapor treatment is considerably desired for the fine control of acidity on the catalysts, technically.

According to the data above, it was attempted to find the relationship between the initial selectivity toward phenol (TOS = 20 min) and acid properties as the existence of big differences for initial selectivity toward phenol, which LAS was set up as a function of initial selectivity toward phenol. Thus, the series of calcined catalysts were utilized in order to verify the exploration. Further data (initial selectivity toward phenol, Lewis acidity) are collected in Table S2. The curves shown in Figure 8 were drawn by the simulation with appropriate parameters based on the suitable equations.



**Figure 8.** Relationship between the amount of Lewis acidity and the initial  $\text{N}_2\text{O}$  selectivity (TOS = 20 min) to phenol. The black points (●) represent H-ZSM-5, Fe-ZSM-5, H-ZSM-5-ST and Fe-ZSM-5-ST; the grey points (★) refer to different temperature calcinated samples.

In Figure 8, the black points (TOS = 20 min) represent H-ZSM-5, Fe-ZSM-5, H-ZSM-5-ST and Fe-ZSM-5-ST catalysts as the black dashed line stands for their linear fit. The gray points (TOS = 20 min) are identified as different temperature calcinated samples, while the short dashed gray line means the linear fit. The red line refers to the linear fit of all the samples mentioned above. Notably, there is a negative correlation between the Lewis acidity and initial selectivity toward phenol. The simulated curve agrees fairly well with the experimental data with the R-square value  $> 0.98$ , which strongly suggests a negative correlation. The amount of LAS to Fe/ZSM-5 is high, as more iron oxide clusters are existed than extra-framework iron ions to achieve invalid catalysis. As a result, the LAS decompose  $\text{N}_2\text{O}$  rather than oxidizing benzene [8,37]. With decreasing LAS, the initial selectivity toward phenol of H-ZSM-5 is clearly higher than that of Fe/ZSM-5, whereas H-ZSM-5 occupies more extra-framework LAS than Fe/ZSM-5 does [43,49]. When the LAS are further reduced, the trend of the selectivity toward phenol keeps increasing. Apparently, H-ZSM-5-ST and Fe/ZSM-5-ST are more active than the other two catalysts. Although the steamed catalysts possess fewer LAS, the extraction of LAS from the framework contributes to a higher initial selectivity [20,42,43,49]. Furthermore, from the carbon calculation in the outlet flow after 3 h (see Table S3). According to our results, the amount of CO and  $\text{CO}_2$  is marginally affected, thus, the CO and  $\text{CO}_2$  can be ignored. From the content of coke, it can probably be speculated catalysts treated with water vapor steam show a better anti-coke ability, which conforms to the literature [20,50]. The samples without steaming exhibit similar anti-coke ability, which are much lower than that of samples with steam-assisted treatment. The samples with higher temperature calcination illustrate tiny lower anti-coke performance because of the lattice destruction [51]. In conclusion, the high temperature steaming treatment is a beneficial method for heightening the initial selectivity toward phenol. Besides, steaming has a strong effect contrasting to the import of Fe species. These data suggest that the initial selectivity toward phenol has a negative correlation with the Lewis acidity.

To validate the above conclusion, a series of calcined catalysts were applied to the oxidation of benzene to phenol. The active trends based on different series of catalysts shown in Figure 8 are very similar to each other. Accordingly, the R-square value is  $> 0.99$ . In contrast to an increase in the amount of LAS as the calcined temperature increases, the initial selectivity toward phenol exhibits a notable decrease. The explanation for this behavior is that a higher calcined temperature causes the

collapse of part of the framework structure, covering the LAS exposed originally [52,53], which results in a decrease of the initial selectivity toward phenol. Therefore, high temperature calcined H-ZSM-5 hinders the reaction due to the presence of more LAS.

Simulated data (see the red line shown in Figure 8) shows that the R-square is ~0.96. As shown, the red line is parallel to the green one. The observation supports our earlier conclusion that there is a negative correlation between the Lewis acidity and initial selectivity toward phenol.

### 3. Materials and Methods

#### 3.1. Preparation of Fe/ZSM-5

The H-ZSM-5 powder with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 25 was kindly provided by Tianjin Nanhua Chemical Co., Ltd., Tianjin, China. Fe/ZSM-5 was prepared by controlled ion exchange of 1 wt.%  $\text{Fe}(\text{NO}_3)_3$  into H-ZSM-5 at 373 K for 3 h followed by filtering, washing three times with demineralized water, drying at 373 K overnight, and finally calcining in static air at 823 K for 4 h.

#### 3.2. Water Steam Treatment

Two g of powdered (60–80 mesh) catalyst was subjected to flowing  $\text{H}_2\text{O}/\text{He}$  ( $1.9 \text{ mL h}^{-1}$ ,  $1800 \text{ mL h}^{-1}$ ) at 923 K for 4 h, followed by flowing He ( $3708 \text{ mL h}^{-1}$ ) at 773 K for 5 h in order to eliminate the impurities adsorbed on the surface of the catalysts. The steam-treated H-ZSM-5 and Fe/ZSM-5 samples are referred to as H-ZSM-5-ST and Fe/ZSM-5-ST, respectively.

#### 3.3. Different Temperature Calcinated Treatment

The commercial H-ZSM-5 powder were calcinated to 773, 873, 973, and 1073 K under the temperature programmed calcination in static air. The samples are donated as H-ZSM-5-773, H-ZSM-5-873, H-ZSM-5-973, and H-ZSM-5-1073, respectively.

#### 3.4. Catalyst Performance in BTOP Reaction

One-step oxidation of benzene to phenol by  $\text{N}_2\text{O}$  was carried out in a fixed-bed stainless steel tube reactor under 698 K and 101 kPa. A feed gas flow, in which the molar ratio of  $\text{C}_6\text{H}_6:\text{N}_2\text{O}:\text{He}$  was 10:1:9, was prepared as follows: the benzene gas was manufactured by flowing liquid benzene into the vaporizing chamber after passing through a brown glass bottle filled with liquid benzene at room temperature, and then was mixed with a  $\text{N}_2\text{O}$  flow in the He atmosphere. Every stream was controlled by a mass flow controller. A total gas flow of  $8640 \text{ mL/h}$  was fed directly into the reactor where 2 g catalyst was loaded [a total weight hourly space velocity (WHSV) of  $4320 \text{ mL g}_{\text{catal}}^{-1} \text{ h}^{-1}$ ]. Before applying the BTOP reaction, the catalyst was treated previously in flowing He at 773 K for 5 h in order to remove impurities adsorbed on the catalyst. Afterwards, the reaction temperature was shifted down to 698 K for BTOP reaction. The products of the liquid and gaseous flow from the outlet of the reactor were detected by a FID detector and a TCD detector. The  $\text{N}_2\text{O}$  conversion has been defined as follows:

$$X_{\text{N}_2\text{O}} = \frac{F_{\text{initial}} - F}{F_{\text{initial}}} \times 100\% \quad (1)$$

where  $F_{\text{initial}}$  and  $F$  are the molar flow rate of the  $\text{N}_2\text{O}$  in the reactor inlet and outlet stream, respectively.

The selectivity and yield for the phenol have been calculated as follows:

$$S_{\text{phenol}} = \frac{F_{\text{phenol}}}{F_{\text{initial}} - F} \times 100\% \quad (2)$$

$$Y_{\text{phenol}} = \frac{F_{\text{phenol}}}{F_{\text{initial}}} \times 100\% \quad (3)$$

where  $F_{\text{phenol}}$  is the molar flow rate of phenol in the reactor outlet stream.

### 3.5. Characterization

XRD measurements were obtained by a Bruker D8 with the Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  nm) in a scanning range of 5–50° at a scanning rate of 10° min<sup>−1</sup> at room temperature. We employed low-voltage high-resolution scanning electron microscopy (LV-HRSEM). The samples were cleaned and refreshed by an Ar ion cleaner placed in the load-lock chamber of the LV-HRSEM instrument at 1 kV for 10 min. All SEM images were taken with the UED detector of a JEOL JSM 7800F GBSH operated at a working distance of a range from 3.4 to 4.7 mm and various magnifications. Surface area and porosity of the samples were determined by N<sub>2</sub> adsorption-desorption at 77 K using a Micromeritics ASAP 2420 V2.09 instrument. BET (Brunner–Emmet–Teller) equation was applied to measure the surface areas ( $S_{\text{BET}}$ ) and the t-plot method was used to determine the micropore volumes ( $V_{\text{micro}}$ ) of all the samples. The mesopore size distribution plots of samples were obtained by the DFT (density functional theory) model applied to the adsorption branches of the isotherms. The UV-vis diffuse reflectance spectra were recorded on a Thermo Evolution 300 UV-vis spectrometer against HZSM-5 zeolite to investigate the nature of the different Fe species in the catalysts. The acid properties were detected by NH<sub>3</sub>-TPD, using AutoChem II 2920 V3.05 and pyridine-FTIR, using Nicolet Avatar 360.

## 4. Conclusions

Through a systematic comparison of water steam treatment of H-ZSM-5 and Fe/ZSM-5 powder, we have illustrated that acidic and mesoporous properties show a significant effect on benzene hydroxylation to phenol. The H-ZSM-5-ST and Fe/ZSM-5-ST exhibit an elimination of strong BAS and LAS, a rather low amount of BAS and a reduction in the number of LAS, and an increase of the mesopore volume ascribed to the hydrothermal treatment, which benefits the reaction.

We approached the preparation of Fe/ZSM-5-ST with a salient decrease of the density of acidic sites and the ratio of B/L by ion-exchange and water steam treatment. Fe/ZSM-5-ST achieves an almost 80% yield of phenol at the initial reaction stage. Moreover, it reveals a relatively high N<sub>2</sub>O conversion and phenol selectivity. Our results have shown that N<sub>2</sub>O has a closer correlation with the Fe species than that with the acid properties, and the reduced LAS property is strongly superior to that of the Fe species, and there is a negative correlation between the Lewis acidity and initial selectivity toward phenol.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/9/1/44/s1>, Figure S1: XRD patterns of (a) H-ZSM-5-773, (b) H-ZSM-5-873, (c) H-ZSM-5-973 and (d) H-ZSM-5-1073, Figure S2: Pyridine FT-IR spectra on (a) H-ZSM-5-773, (b) H-ZSM-5-873, (c) H-ZSM-5-973 and (d) H-ZSM-5-1073, Table S1: Acidity properties from Py-IR analysis for catalysts H-ZSM-5-773, H-ZSM-5-873, H-ZSM-5-973 and H-ZSM-5-1073, Table S2: Benzene oxidation to phenol with N<sub>2</sub>O after 20 min of the reaction, Table S3: Carbon calculation in the outlet flow after 3 h reaction time for samples.

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