



# Highly selective synthesis of *para*-cresol by conversion of anisole on ZSM-5 zeolites



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## ABSTRACT

A novel route to obtain the high *para*-selectivity was developed by conversion of anisole on modified ZSM-5 in a continuous flowing fixed-bed reactor. It showed that the silylation and steaming treatment were significantly beneficial to enhance the *para*-selectivity. Compared with the parent catalysts, the *para*-selectivity was sharply increased from 18.13% to 69.21% after the second silylation, which was further increased to 80.67% by steaming treatment. The acid sites with different strength of catalysts were studied by NH<sub>3</sub>-TPD which had an influence on both the *para*-selectivity and the amount of aromatics in the products.

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## 1. Introduction

*Para*-cresol is an important intermediate in the formation of antioxidants and preservatives for plastics, pharmaceuticals, herbicides, agrochemicals and dyes [1]. Now, the industrial process of producing *para*-cresol is sulpho alkaline fusion of toluene that causes corrosion and disposal of waste water and solid residue. With a green process, cresol can be formed in the alkylation of phenol with methanol on solid catalyst such as HZSM-5, BETA, HMCM-22 zeolites and usually the mixed cresol were produced [1–5]. Metal oxide catalysts such as Fe<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, CuO/Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and CeO<sub>2</sub> have been reported to selectively alkylate phenol with methanol, which essentially produced *ortho*-cresol and 2,6-xyleneol [6–16].

Because the functional group –OH of phenol is smaller than –CH<sub>3</sub> group of toluene in size. It is difficult to obtain the higher *para*-selectivity in alkylation of phenol with methanol compared with that of toluene. Previous studies [2,17,18] have reported that cresol was produced by anisole on solid acids, probably reflecting that anisole was a more effective alkylating agent than methanol [19]. Grabowska [20] studied transformation of anisole over metal oxides catalysts on which *ortho*-cresol and 2,6-xyleneol were obtained while *para*-cresol was not detected in the products. Besides, the conversion of anisole was also studied

as a model reaction which aims to eliminate the phenolic compounds in bio-oils [21–24].

We proposed a novel route to obtain the high *para*-selectivity by alkylation phenol with methanol. In the first step, phenol was etherificated with methanol on the solid catalyst and anisole was produced. In the second step, the high *para*-selectivity was obtained by conversion of anisole over selective catalysts. At the same time, the produced phenol was return to the first step to react with methanol.

The first step of phenol etherificate with methanol was easy to obtain the 100% selectivity of anisole [25]. However, data is still scarce in highly selective synthesis of *para*-cresol by conversion of anisole on zeolites. In this paper, the second step (Scheme 1) was studied and the high *para*-selectivity was obtained by conversion of anisole on modified ZSM-5. It shown that the *para*-selectivity sharply increased by treatment of silylation and steaming.

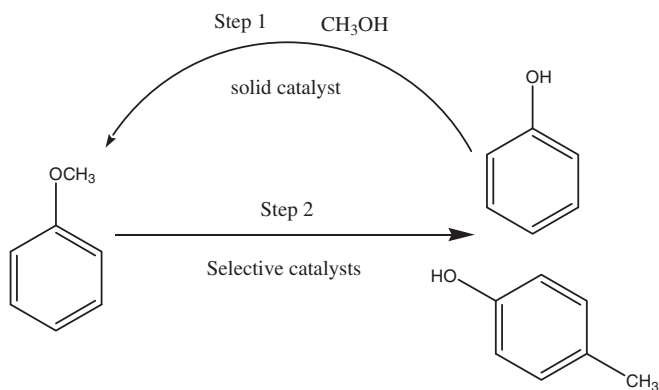
## 2. Experimental

### 2.1. Catalytic materials

HZSM-5 zeolite samples were purchased from Nankai University Catalyst Co., Ltd, China. The crystal size was 1–2 μm and the molecule ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was 30. HZSM-5 zeolite (100 g) was bonded with silcasol in which the percentage of silca was 30% and then the samples were dried at 120 for 8 h and calcined at 600 °C for 3 h. This sample was sliced into 3–5 mm cylindrical that

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**Scheme 1.** The route of high *para*-cresol by alkylation phenol with methanol.

was denoted as HZ. The HZ (3.0) was impregnated in 2.6 ml solution of phenyl methyl diphenyl silicone oil in cyclohexane with the weight percentage of 50%. After it had impregnated at room-temperature for 8 h, and then calcined at 600 °C for 3 h and was denoted as SiHZ-1. Repeated the procedure of preparation once again based on SiHZ-1, the SiHZ-2 was obtained. SiHZ-2 was under 100% steam stream for 3 h at 500 °C and then calcined at 600 °C for 3 h. This sample was denoted as S-SiHZ-2.

## 2.2. The characterization of acid site and SEM

NH<sub>3</sub> adsorption and Temperature Programmed Desorption (NH<sub>3</sub>-TPD) on samples was studied using AutoChem2910 chemical adsorber instrument. Physically adsorbed NH<sub>3</sub> was removed by helium at 100 °C until further weight loss was not observed. NH<sub>3</sub>-TPD of the sample was carried out by heating the sample at a rate of 10 °C/min from 100 to 600 °C. The effluent stream was monitored continuously with a Thermal Conductivity Detector (TCD) to determine the rate of ammonia desorption. SEM photograph of parent ZSM-5 was taken on a KYKY-1000B to estimate crystal sizes.

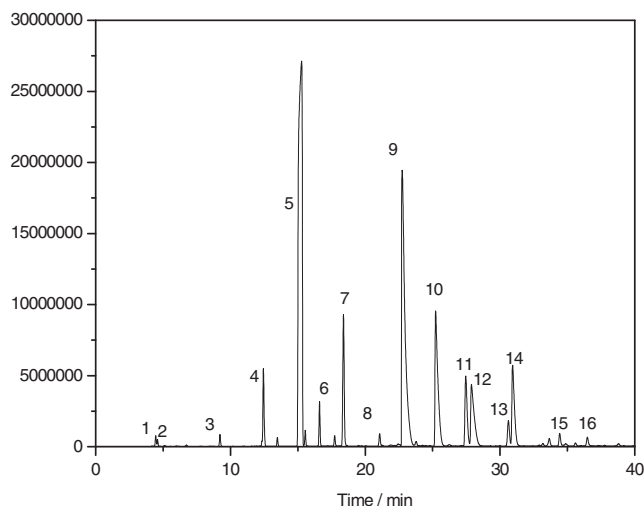
## 2.3. Catalytic reaction

Catalytic reactions were carried out in a continuous flowing fixed-bed reactor at 400 °C at atmospheric pressure with a WHSV 3.0 h<sup>-1</sup> and the catalysts were 3.0 g. The molecular ratio of water and anisole was 4. Reaction products were analyzed online using Agilent GC7890 with a capillary column of CRESOL and flame ionization detector. The collected products also analyzed by GC-MS with Agilent GC7890 (capillary column of CRESOL) and MS5975C. The conversion of anisole was defined as 100 minus the percent of anisole in products. The *para*-selectivity was the percent of *para*-cresol in three isomers of cresol. The selectivity of cresol was the weight percent of in products divided by conversion of anisole.

## 3. Results and discussion

### 3.1. Reaction performance and reaction net

The reaction products over HZ were collected after 5 min with reaction temperature 400 °C which were analyzed by GC-MS that aromatics included toluene, xylene and mesitylene and methylanisole (Fig. 1). The reaction net of anisole included the disproportionation of anisole and dealkylation of anisole forming phenol and olefins [3] as well as rearrangement of anisole yielding cresol [18].



**Fig. 1.** The GC-MS results of reaction products. (1) Dimethyl ether, (2) methanol, (3) Toluene, (4) Xylene, (5) Anisole, (6) Mesitylene, (7) 4-Methylanisole, (8) 2-Methylanisole, (9) Phenol, (10) *O*-Cresol, (11) *P*-Cresol, (12) *M*-Cresol, (13) 2,5-dimethyl-phenol, (14) 2,3-dimethyl-phenol, (15) 3,4-dimethyl-phenol, (16) 2,4,5-trimethyl-phenol.

**Table 1**

The products distribution in conversion of anisole at different reaction temperature on HZ.

Organic products (wt.%) <sup>a</sup>	Reaction temperature			
	300 °C	350 °C	400 °C	450 °C
Methanol	0.54	1.33	2.07	1.73
Dimethyl ether	0.83	1.37	1.49	1.29
Aromatics	0.02	0.11	0.88	0.97
Anisole	79.98	70.80	47.85	34.99
Methylanisole	1.40	3.14	4.50	4.30
Phenol	15.13	18.98	29.35	31.56
<i>Orth</i> -cresol	1.25	2.30	6.10	9.08
2,6-xylene	0.00	0.00	0.00	0.13
<i>Para</i> -cresol	0.61	0.96	2.61	3.67
<i>M</i> -cresol	0.25	0.45	2.66	5.99
2,4-xylene	0.00	0.12	0.42	0.96
Others	0.00	0.30	2.07	4.93
Conversion of anisole (wt.%)	20.02	29.20	52.15	65.01
Selectivity of cresol (wt.%)	10.53	12.68	21.82	28.82
Phenol/cresol <sup>b</sup>	8.25	5.89	2.96	1.94
<i>Para</i> -selectivity <sup>c</sup>	29.05	25.82	22.97	19.58

<sup>a</sup> The results of reacted 60 min.

<sup>b</sup> Phenol/cresol was the molecule ratio of phenol to cresol in the products.

<sup>c</sup> *Para*-selectivity was the percent of *para*-cresol in cresol.

Table 1 shows the products distribution in conversion of anisole over HZ at 300, 350, 400 and 450 °C, respectively. We can see that phenol was five times of cresol in the conversion of anisole at lower reaction temperature such as 300 and 350 °C. *Para*-cresol in equilibrium composition of isomer mixtures was 14% on USY [26] and 16% on ZSM-5 [27] at 380 °C, respectively. In this study, the *para*-selectivity increased with the decrease in the reaction temperature. It showed that the *para*-selectivity was 22.97%, exceeding equilibrium composition of isomer mixtures (14%), which perhaps arose from coking selectively passivated the external acid site of HZ in the process of reaction. The *para*-selectivity did not increase obviously even the weight velocity increase to 100 h<sup>-1</sup> (see Supplementary material Fig. S1).

With increase of reaction temperature, the conversion of anisole increased while the ratio of phenol and cresol decreased in the products. However, phenol was the main products which implied that

the massive hydrolysis of anisole was carried out in the process of reaction. In other words, the reaction of anisole hydrolysis predominates on acid catalysts. The product of hydrolysis was methanol which alkylated with phenol and yielded cresol and water as well as xylenol. Based on discussed above, the reaction net of anisole in the ZSM-5 was proposed which differed from Refs. [3,18] (Scheme 2). Phenol and methylanisole were produced by disproportionation of two anisole molecules. Methylanisole reacted with phenol yielding two cresol molecules or produced phenol and xylenol.

As is well known, the acid sites located in the vicinity of pore openings of ZSM-5 were the accessible acid sites for some aromatic molecule [28]. The amount of internal acid sites was larger than that of external acid sites on microscale ZSM-5. Anisole was hydrolyzed on both the internal acid sites and the external acid sites. Alkylation of methanol with phenol was carried on the internal acid sites of ZSM-5 which produced the *para*-selectivity in the constraint channel and the aromatics was also produced by methanol. On the other hand, anisole was hydrolyzed on the unconstraint external acid sites on which methanol were formed and further reacted to yield dimethyl ether.

### 3.2. Enhance *para*-selectivity by silylation

The reaction performance of samples was showed in the Table 2. The conversion of anisole on SiHZ-1 sharply decreased compared with that of parent catalyst HZ while the *para*-selectivity increased slowly from 18.13% to 29.16%. With the second silylation based on SiHZ-1, the conversion of anisole on SiHZ-2 decreased slightly while the *para*-selectivity sharply increased from 29.16% to 69.28%. This indicated that the second silylation seriously narrowed the pore-opening size and reduced the external acid sites which contribute to the high *para*-selectivity. Silylation was widely used to eliminate the external acid site and reduce the pore opening of ZSM-5 zeolites by using different organic silicon compounds and various methods [29–32]. The enhancement of *para*-selectivity was ascribed to the decrease in pore-opening size and the inactivation of external acid sites [33,34]. It is difficult to study the pore-opening size and the external surface acid sites individually because they are often correlated to each other. So, in this study, the high *para*-selectivity on SiHZ-2 was also attributed to narrow the pore-opening size and to passivate the external surface acid sites.

**Table 2**

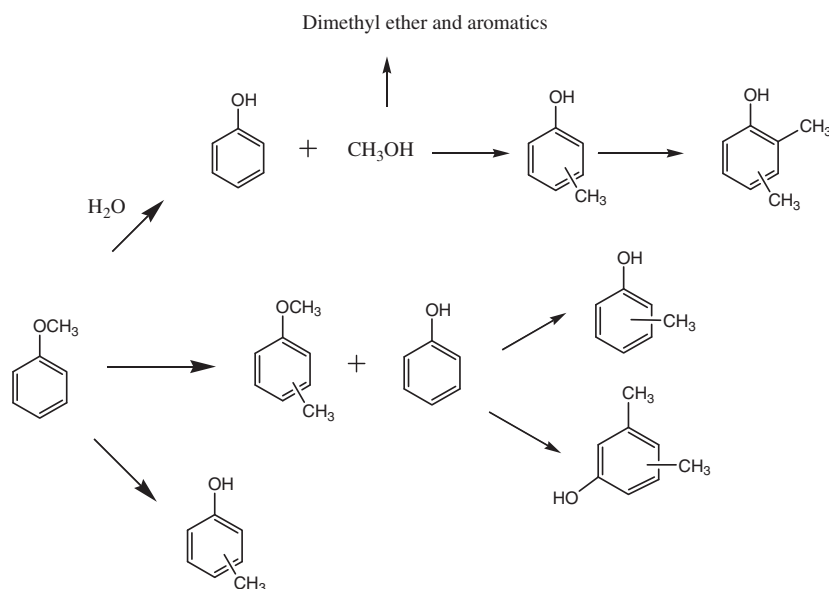
The products distribution in conversion of anisole at different samples.

Organic products (wt.%) <sup>a</sup>	HZ	SiHZ-1	SiHZ-2	S-SiHZ-2
Methanol	0.25	1.16	1.23	0.70
Dimethyl ether	1.47	1.04	2.36	0.12
Aromatics	9.10	1.35	2.73	1.84
Anisole	27.49	51.72	68.17	86.59
Methylanisole	1.54	1.81	1.53	0.29
Phenol	27.19	22.87	17.14	7.57
O-cresol	9.32	6.10	1.00	0.28
2,6-xylenol	0.24	0.06	0.00	0.00
<i>P</i> -cresol	4.39	3.19	3.98	1.97
<i>M</i> -cresol	10.50	4.80	0.77	0.20
2,4-xylenol	2.03	0.54	0.08	0.00
Others	6.50	5.37	1.01	0.45
Conversion of anisole (wt.%)	73.09	48.29	31.83	13.41
Selectivity of cresol (wt.%)	32.41	22.63	18.07	18.21
<i>Para</i> -selectivity <sup>a</sup>	18.13	29.16	69.21	80.67

<sup>a</sup> Results of reacted 5 min; reaction temperature 400 °C.

### 3.3. Enhance *para*-selectivity by steaming treatment

SiHZ-2 was treated with pure steam at temperature 500 °C for 3 h S-SiHZ-2 to obtain the reaction performance was showed in the Table 2. The conversion of phenol as sharply decreased from 31.83% to 13.41% while the *para*-selectivity significantly increased with steaming treatment from 69.21% to 80.67%. The *para*-selectivity was increased with enhancement of the feed of W/F while the conversion of anisole had an obvious decrease (see Supplementary material Fig. S2). Steaming treatment techniques have been developed for removing part of aluminum species in zeolite frameworks with the aim of decreasing the acidity and adjusting channel of ZSM-5. Zhang [35] reported that the increase of DMN selectivity in the methylation of 2-methylnaphthalene with methanol was attributed to narrow the pore size of ZSM-5 and reduce external acid sites by hydrothermal (steam) treatment and silylation methods, which limited isomerization of 2-MN and further alkylation of DMN once it was formed. In this study, the *para*-selectivity was increased by steaming treatment. The newly formed Si–O–Si bonds on the surface after silylation were reconstructed under the steaming treatment which both passivated the external acid sites and narrow the pore size of ZSM-5.



**Scheme 2.** The reaction net of anisole on ZSM-5.

### 3.4. Para-selectivity and acid sites

Fig. 2 shows the acid sites distribution of samples. Two desorption peaks were observed for aluminosilicates zeolite, in which the LT (lower temperature desorption) peak appeared at 250 °C mainly consisted of the acid sites with strength  $H_0$  range from  $-3.0$  to  $+2.27$  and the HT (higher temperature desorption) peak mainly consisted of the acid sites with strength  $H_0 \leq -3.0$  for strong chemisorbed [36]. In this study, both the LT peak and HT peak of SiHZ-2 sharply decreased compared with the parent samples. The proportion of external acid sites in total acid sites was only 10% on the microscale HZSM-5 (1–2  $\mu\text{m}$ ) [28]. In this study, the crystal size of parent ZSM-5 was approximately 1–2  $\mu\text{m}$  (Fig. 3). This implied that the silylation passivated both the external and the internal acid sites of ZSM-5. The acid sites of S-SiHZ-2 were decreased slightly by steaming treatment of silylated catalysts SiHZ-2.

The HT peak area of SiHZ-2 sharply decreased while its LT peak area had a moderate decrease which indicated that the strong acid sites were easily to eliminate on ZSM-5. Combined the reaction performance (Table 2) with the results of  $\text{NH}_3$ -TPD, both silylation and steaming treatment decreased the acid sites of external acid sites which contributed to the enhancement of *para*-selectivity.

Besides, the percentage of aromatics in the products was about 9% after 5 min which decreased to 0.88% after 30 min. Toluene and xylene were the main aromatics products (Fig. 2) which were produced by methanol. The strong acid sites of fresh catalyst contributed to convert methanol to aromatics. In our previous study, the strong acid sites were easily passivated by the reaction stream [36]. In the process of reaction, the strong acid sites were covered by aromatic coke species which contributed to the decrease of aromatics. This indicated that the moderate acid strength was beneficial to synthesis cresol by anisole.

Kubo et al. studied the process of  $\text{Si}(\text{OH})_4$  molecules chemical vapor deposition on the ZSM-5 (010) surface by the molecular dynamics (MD) method and concluded that the new Si–O–Si bonds was formed on the surface. The constructed  $\text{SiO}_2$  layer was not amorphous, but inherited the ZSM-5 structure [37]. So the newly formed Si–O–Si bonds contribute to the decrease in the acid sites of both on the external and on the vicinity of pore openings of ZSM-5. Based on this, we tentatively proposed the selective model on ZSM-5 zeolites as Scheme 3. As shown in Scheme 3, the formed *ortho*-cresol and *meta*-cresol in the intersection of ZSM-5 channel which slowly diffuse out of the channel and the *para*-cresol easily diffuse out of the channel. *Para*-cresol diffused out of the channel

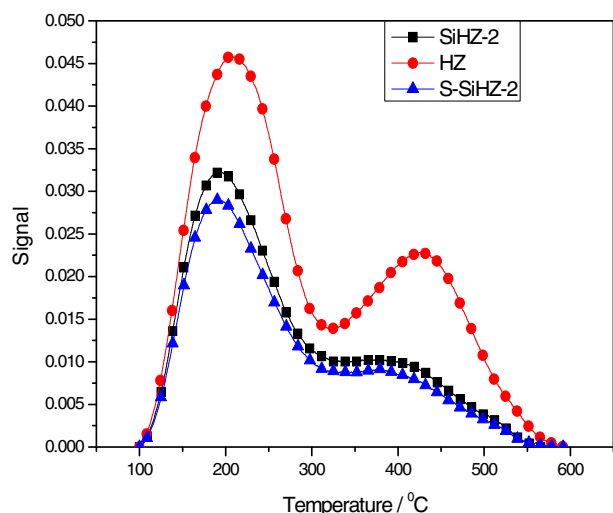


Fig. 2. The  $\text{NH}_3$ -TPD curves of samples.

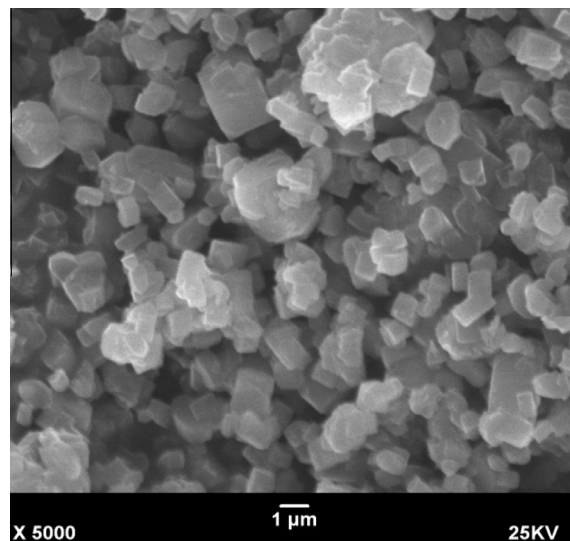
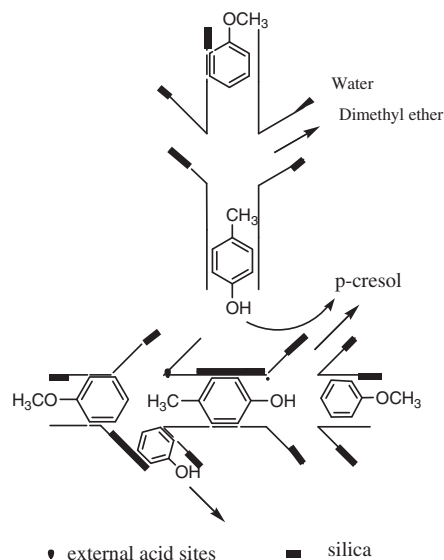


Fig. 3. SEM of parent ZSM-5.



Scheme 3. The selective model on the ZSM-5 zeolites.

as the final products when the concentration of external acid sites was very low and the possibility of *para*-cresol isomerization decreased. The *para*-selectivity will be enhanced when the external acid sites were passivated and at the same time the pore opening size decreased.

## 4. Conclusion

A new route to obtain the high *para*-cresol by alkylation phenol with methanol was proposed. In the reaction net of anisole, the hydrolysis of anisole predominates over acid catalysts, and then the product of hydrolysis was methanol which alkylation with phenol yielded cresol and water as well as xylenol. The high *para*-selectivity of 80.67% was obtained by silylation and steaming treatment. The enhancement of *para*-selectivity by silylation and steaming treatment was ascribed to the decrease in pore-opening size and the inactivation of external acid sites. The strong acid sites of catalyst contribute to convert phenolic compound to aromatics while moderate acid strength was beneficial to synthesis cresol by anisole.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.micromeso.2013.11.007>.

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