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Catalytic cleavage of C–O linkages in benzyl phenyl ether assisted by microwave heating†

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The microwave-assisted cleavage of C–O linkages in benzyl phenyl ether was investigated at 200 °C in the presence of ZrP or SBA-15 doped with or without metal catalyst (Pd/C or Ru/C). The total yield of phenol and benzyl alcohol from benzyl phenyl ether depolymerization with ZrP was 26.91%, while the yield of phenol reached 26.11% for that with Pd/C. Hybrid catalysts performed effectively for promoting the formation of phenol. A conversion of 85.70% was achieved with ZrP–Pd/C catalyst, and the selectivity to phenol reached 47.32%. The highest yield of phenol was obtained at 1 h, and repolymerization was remarkable at longer reaction time. Based on the reaction using phenol and benzyl alcohol as the reactants, benzyl phenyl ether might be decomposed into phenol and benzyl alcohol following with the repolymerization producing thermally stable polymers in the presence of Pd.

1. Introduction

Biomass is the only renewable resource for the production of liquid fuels and chemicals.[1] As one of the three main components of biomass, lignin is a potential feedstock to be converted into aromatics and phenolic compounds due to its abundant methoxylated phenyl-propane units connected with C–O and C–C bonds.[2–4] Lignin can be converted by various thermal–chemical ways and hydrothermal is a promising way to produce liquid products.[5–9] Extensive studies have been carried out on the hydrothermal degradation of various lignins, and most of these studies were conducted under electric heating.[5,10–13]

These days, microwave heating have drawn increasingly attention in terms of biomass and lignin conversion, due to its cost-effective heating compared with electric heating.[14–18] Despite these work, the degradation mechanism of lignin is not clear yet. One main reason is that the complex structure of real lignin usually lead to a wide range of product distribution.[2] In this work, benzyl phenyl ether is selected as the model compound to give insight into the cleavage mechanism of α-O-4 bond which is one of the main ether bonds in real lignin.[19–22]

Catalyst plays a vital role in the conversion of lignin. Roberts *et al.* reported that the conversion of benzyl phenyl ether without catalyst took 4 h to reach 91% at 270 °C.[19] When catalysts were used, efficient cleavage of C–O bonds can be fulfilled under mild conditions. He *et al.* reported that the conversion of benzyl phenyl ether with Ni/HZSM-5 reached about 97% after 100 min at 250 °C.[20,21] Park *et al.* investigated the degradation of benzyl phenyl ether with Pd catalyst supported on cesium-exchanged heteropolyacid, reporting a conversion of 78% after 1 h at 200 °C, with phenol, benzene and toluene as the main products.[23] These literatures confirmed that catalyst is important for promoting the conversion.

The target of this work is to investigate the microwave-assisted cleavage of C–O linkages in benzyl phenyl ether catalyzed by ZrP or SBA-15 doped with or without metal catalyst (Pd/C or Ru/C). As a solid catalyst, ZrP performs well for ether bonds cleavage in conversion of xylose and glucose.[24,25] SBA-15 is widely used as catalyst support due to its large surface area and uniform tubular mesopores.[26] Metal catalysts of Pd/C and Ru/C were reported as good catalysts for lignin and biomass conversion.[27,28] The reactions of phenol and benzyl alcohol which are the possible intermediate products were carried out to further study the conversion pathway of benzyl phenyl ether.

2. Materials and methods

2.1. Materials

The solvents used in the study were purchased from Nanjing Reagent Co. and used as received. 5 wt% Ru/C catalyst and 5 wt% Pd/C catalyst were purchased from Aladdin. SBA-15 was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Benzyl phenyl ether (>98%, GC assay) was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). $NH_4H_2PO_4$ and $ZrOCl_2\cdot 8H_2O$ were purchased from Sinopharm chemical reagent Co., Ltd.

2.2. Preparation and characterization of catalysts

The zirconium phosphate catalyst (ZrP) was prepared according to the published work.[29] In brief, $NH_4H_2PO_4$ (1 mol L^{-1}, 200 mL) was added to $ZrOCl_2\cdot 8H_2O$ (1 mol L^{-1}, 100 mL) at the P/Zr mole

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ratio of 2. The solution was stirred for 30 min. The precipitate was filtered and washed with deionized water until the pH of 5, dried at 100 °C overnight, and then calcined at 400 °C for 4 h in air.

Ammonia temperature-programmed desorption (NH_3-TPD) was carried out on a quartz U-tube apparatus. The 40–60 mesh sample (0.1 g) was firstly degassed in a He stream at 400 °C for 30 min. Then the temperature was cooled down to 100 °C and 5% NH_3/N_2 was used for adsorption under a flow of 20 mL min^{-1} for 0.5 h. After that, pure He was switched to remove any physically adsorbed NH_3 for 0.5 h under the same temperature. Desorption of NH_3 was performed from 100 °C to 700 °C at a rate of 10 °C min^{-1} and the temperature was held at 700 °C for another 1 h. The desorbed NH_3 was measured using a gas chromatograph (GC-SP6890) with a thermal conductivity detector (TCD). XRD was performed on a D/max rC X-ray diffractometer using Cu Kα radiation from 5° to 80° with a step of 0.02° per s.

2.3. Depolymerization of lignin

The hydrothermal degradation of benzyl phenyl ether was conducted in a microwave reaction system (MDS-6, Sineo, China). The 70 mL vessel was made of Teflon, with a maximum working condition of 4 MPa and 220 °C. In a typical run, 0.2 g benzyl phenyl ether and 0.1 g ZrP or SBA-15 doped with or without 0.1 g Pd/C or Ru/C were loaded into the reactor vessel with 15 mL deionized water. Then the reactor was heated by microwave irradiation to 200 °C in three steps (three minutes to 160 °C, three minutes to 180 °C and three minutes to 200 °C). After keeping at 200 °C for a desired time, the reactor was cooled to room temperature by forced-air. Each reaction condition was repeated at least twice.

After reaching the room temperature, the reactor was opened, and all liquid and solid products were collected. The reactor was rinsed with ethyl acetate, then the ethyl acetate was added into the collected products. The liquid product was separated from the solid catalysts by filtration. The obtained liquid product was then extracted with ethyl acetate three times, and the ethyl acetate extracted liquid product was calibrated to 100 mL by adding ethyl acetate for further GC and GC MS analysis.

2.4. Characterization of the products

The liquid products were identified by GC-MS (Agilent 7890A-5975C). The condition of GC MS was set to be: the injector temperature was kept at 300 °C; the chromatographic separation was performed with a HP-5 MS capillary column; the oven temperature was programmed from 40 °C (3 min) to 180 °C (2 min) with 5 °C min^{-1} heating rate, and then to 280 °C (2 min) with 10 °C min^{-1} heating rate; the mass spectra were operated in EI mode at 70 eV. The mass spectra were obtained from *m*/*z* 50 to 650. The chromatographic peaks were identified according to the NIST MS library and previously published work.[30,31] The yield of product i (mass yield, Y_i) was quantified by GC (Shimadzu 2014) with an AT.SE 54 capillary column and a FID detector, and calculated as:

$$Y_{\mathrm{i}}(\%) = \frac{m_{\mathrm{i}}}{m_{\mathrm{bpe\_0}}} \times 100\% \tag{1}$$

where m_{i} is the mass of product i, $m_{\mathrm{bpe\_0}}$ is the initial mass of benzyl phenyl ether.

The conversion (C) was determined by the weight difference of benzyl phenyl ether before and after reaction, and was calculated as:

$$C(\%) = \frac{m_{\mathrm{bpe\_0}} - m_{\mathrm{bpe}}}{m_{\mathrm{bpe\_0}}} \times 100\% \tag{2}$$

where m_{bpe} is the mass of benzyl phenyl ether after reaction.

The selectivity (S_{i}) was calculated as:

$$S_{\mathrm{i}}(\%) = \frac{Y_{\mathrm{i}}}{C} \times 100\% \tag{3}$$

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1 shows the NH_3-TPD desorption profiles of ZrP and SBA-15. One strong broad desorption peak could be observed for ZrP from 570 to 660 °C, indicating the existence of strong acid site. SBA-15 was reported with no acid sites. However, one small broad desorption peak could be found around 550 °C for SBA-15 in the present work. The weak peak may be attributed to

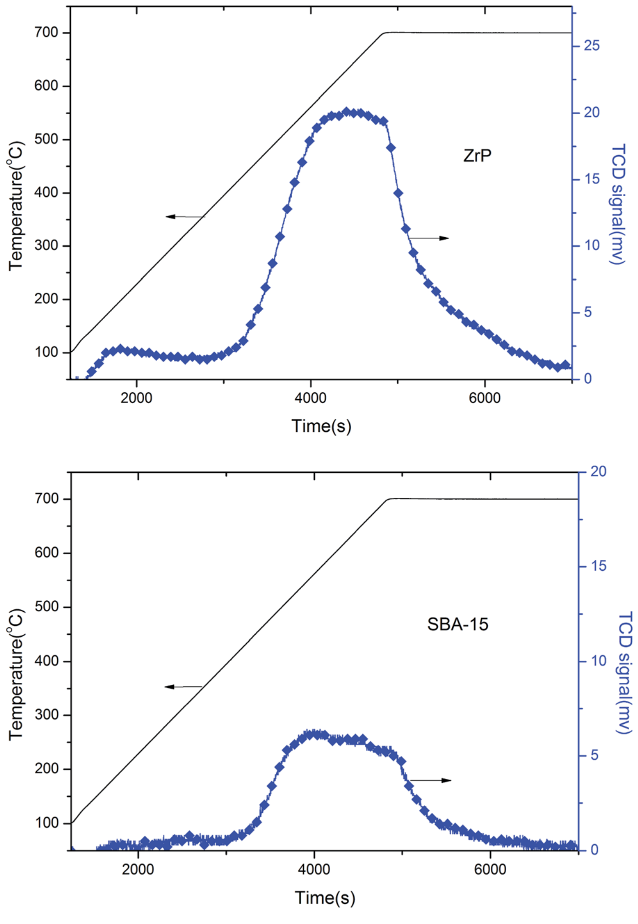

Fig. 1 NH_3-TPD desorption profiles of ZrP and SBA-15.

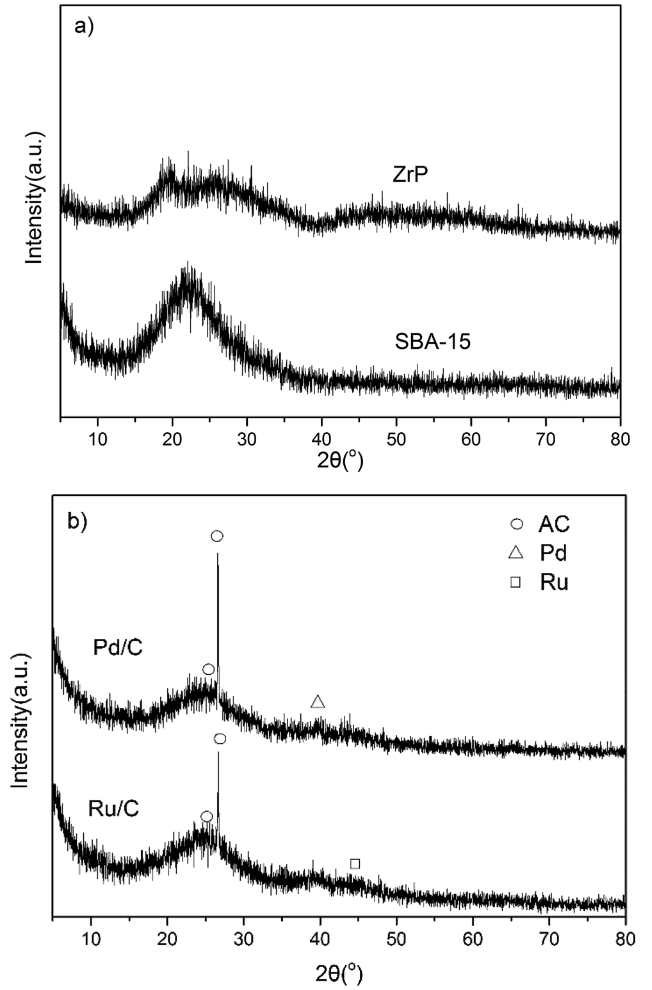

Fig. 2 X-ray diffractogram patterns of ZrP, SBA-15(a) and Pd/C, Ru/C(b).

the existence of silanols.[32] The absolute peak area of the NH_3-TPD desorption profile is considered to be linear with the amount of its acid sites.[25] Calculated based on the peak area, ZrP possessed the acid sites of 0.2175 mmol g^{-1}.

The X-ray diffractogram (XRD) patterns of ZrP, SBA-15, Pd/C and Ru/C are shown in Fig. 2. For ZrP catalyst, two broad peaks in 2θ range of 15–40° and 40–70° indicated its amorphous nature, which was consistent with the published work.[24,25] SBA-15 also exhibited amorphous structure with one strong broad peak in the range of 2θ from 20° to 40°. For the two metal catalysts supported on activated carbon, one board peak around 24° could be observed and this peak corresponded to the amorphous carbon. The Ru crystallite peak at $2\theta = 44°$ and Pd crystallite peak at $2\theta = 39.34°$ were very weak, indicating that both Ru and Pd particles were well dispersed on the support (particle size less than 5 nm).[33,34]

3.2. Effect of temperature

Fig. 3 is the product yields of benzyl phenyl ether at different temperatures without catalyst. The main products were phenol and benzyl alcohol. Only 0.10% and 0.38% yield of phenol were obtained at 150 °C and 180 °C, respectively. At 200 °C, the yields of phenol and benzyl alcohol reached 4.07% and 2.74%, respectively. Degradation at higher temperature cannot be investigated in this system because of the working condition limitation.

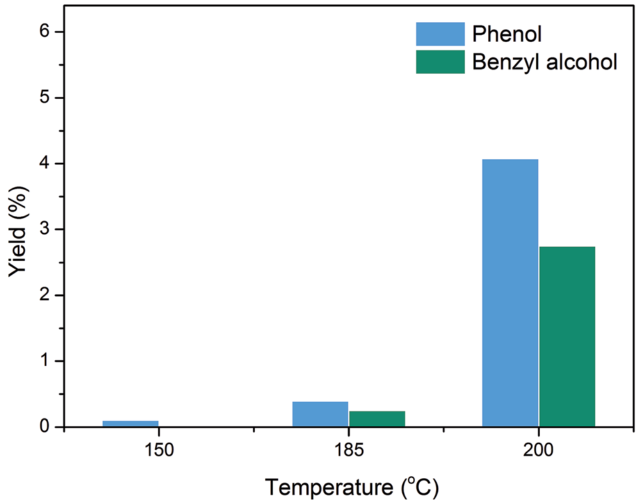

Fig. 3 Product yields of benzyl phenyl ether without catalyst. Reaction conditions: 0.2 g benzyl phenyl ether, 15 mL H_2O, 1 h.

3.3. Effect of catalyst species

Benzyl phenyl ether can be partially degraded at 200 °C without catalyst, but the product yields were low. Therefore, ZrP, SBA-15, Pd/C and Ru/C were screened to promote the conversion. The conversions of benzyl phenyl ether with different catalysts are given in Table 1. The conversion with the treatment of ZrP was 59.93%. While the conversion with SBA-15 was only 45.27%. The presence of metal catalysts resulted in higher conversions. Conversions with Pd/C and Ru/C were 85.51% and 72.66% respectively (Table 1).

As listed in Table 1, higher product yields were obtained with all catalysts compared to that without catalyst. The main products identified by GC MS were phenol, benzyl alcohol and toluene. Roberts *et al.* studied the products of benzyl phenyl ether under electric heating with LDI-TOF/MS, and reported that dimers and trimers could also be found in the products.[19] The highest yields of phenol (13.29%) and benzyl alcohol (13.62%) were obtained with ZrP. Only 8.59% yield of phenol and 5.33% yield of benzyl alcohol were produced over SBA-15. For the metal catalysts, 8.07% yield of phenol and 2.68% yield of benzyl alcohol were obtained with the application of Ru/C. Although no benzyl alcohol was produced over Pd/C, the yield of phenol reached the highest value of 26.11% (Table 1).

3.4. Effect of hybrid catalysts

ZrP or SBA-15 was mixed with Ru/C or Pd/C to investigate the performance of hybrid catalysts, and the conversions with different hybrid catalysts are given in Table 2. Low conversion of 47.87% and 50.02% were obtained over SBA-15–Ru/C and ZrP–Ru/C, respectively. The application of ZrP–Pd/C resulted in the highest conversion of 85.7%.

Table 1 Product yields and selectivities of benzyl phenyl ether with different catalysts[a]

			Toluene		Phenol		Benzyl alcohol	
Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)
1	ZrP	59.93	0.00	0.00	13.29	22.18	13.62	22.73
2	SBA-15	45.27	0.00	0.00	8.59	18.98	5.33	11.77
3	Pd/C	85.51	2.75	3.18	26.11	30.18	0.00	0.00
4	Ru/C	72.66	0.00	0.00	8.07	11.10	2.68	3.69

[a] Reaction conditions: 0.2 g benzyl phenyl ether, 0.1 g catalyst, 15 mL H_2O, 200 °C.

The yields of phenol and benzyl alcohol over SBA-15–Ru/C were 7.8% and 0.95%. And the yields of these two products over ZrP–Ru/C were 14.26% and 3.78%, respectively. The low yields with Ru/C as the metal catalyst indicates that the promotion of Ru/C is not as strong as Pd/C. The yield of phenol with the treatment of SBA-15–Pd/C was 28.55%. 2.11% yield of toluene was identified as well, while no benzyl alcohol was identified. When ZrP and Pd/C were used as the hybrid catalyst, 40.55% yield of phenol was obtained with the selectivity of 47.95%. The yield of phenol over ZrP–Pd/C was higher than that using ZrP (13.29%) or Pd/C (26.11%).

The hydrothermal stability of catalyst in aqueous phase condition is an important aspect. The X-ray diffractogram (XRD) patterns of spent ZrP and spent Pd/C are shown in Fig. S1.† The pattern of spent ZrP showed no difference compared to that of fresh ZrP, showing that ZrP was stable in terms of the crystalline structure in aqueous condition. The pattern of Pd/C also showed a typical amorphous structure of activated carbon without sharp peak of Pd, indicating that the well dispersion of Pd particles remained in the aqueous condition. NH_3-TPD desorption revealed that the acid sites of ZrP decreased slightly to 0.1575 mmol g^{-1} after the reaction. Liao *et al.* observed that catalytic performance of ZrP decreased slightly for conversion of cellulose after the first use.[24] They claimed that this phenomenon was attributed to P leaching under the hydrothermal reaction condition, and P leaching only took place in the first run.

3.5. Effect of reaction time

The effect of reaction time was investigated with ZrP–Pd/C catalyst at 200 °C. The conversion of benzyl phenyl ether and the product yields at 0–4 h were shown in Fig. 4. At 0 h, 41.06% conversion was observed. With the reaction time increasing, the conversion increased, reaching 85.70% at 1 h, and 99.23% at 4 h.

The products of benzyl phenyl ether degradation were phenol and toluene. At 0 h, 6.30% phenol was obtained. The highest yield of phenol was obtained at 1 h as 41.55%. After that, the yield decreased slightly to 41.38% at 2 h and 39.97% at 4 h. Toluene reached the highest yield of 1.22% at 2 h. The results indicates that most of the benzyl phenyl ether has been consumed in 1 h with the treatment of ZrP–Pd/C. Longer reaction time to 4 h resulted in the decreasing of product yields, although the conversion is higher. This should be the result of repolymerization reaction.

3.6. Chemical pathways for the formation of primary products

According to He *et al.*'s report, the mole yields of phenol and benzyl alcohol formed from the depolymerization of benzyl phenyl ether catalyzed by Ni/HZSM-5 under electric heating exhibited a stoichiometry balance.[21] Therefore, they proposed a hydrolysis reaction mechanism for the decomposition of benzyl phenyl ether. However, no obvious stoichiometry balance was found for phenol and benzyl alcohol in the present work. The mole yield of phenol was generally higher than that of benzyl alcohol. With Pd/C as the catalyst, benzyl alcohol was not identified in the liquid products. And the total yield of products identified by GC was lower than the calculated conversion. One possibility is that the products formed by hydrolysis reaction reacted further to form some secondary products which could not be identified by GC. To test the possibility, phenol and benzyl alcohol which might be the possible primary products were used as the reactants to investigate if some further reaction existed in our reaction system. Product yields and selectivities of phenol

Table 2 Product yields and selectivities of benzyl phenyl ether with hybrid catalysts[a]

			Toluene		Phenol		Benzyl alcohol	
Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)
1	SBA-15-Ru/C	47.87	0.10	0.21	7.80	16.30	0.95	1.98
2	SBA-15-Pd/C	78.76	2.11	2.68	28.55	36.24	0.00	0.00
3	ZrP–Ru/C	50.02	0.35	0.70	14.26	28.52	3.78	7.56
4	ZrP–Pd/C	85.70	0.96	1.12	40.55	47.32	0.00	0.00

[a] Reaction conditions: 0.2 g benzyl phenyl ether, 0.1 g SBA-15 or ZrP catalyst and 0.1 g metal catalyst, 15 mL H_2O, 200 °C.

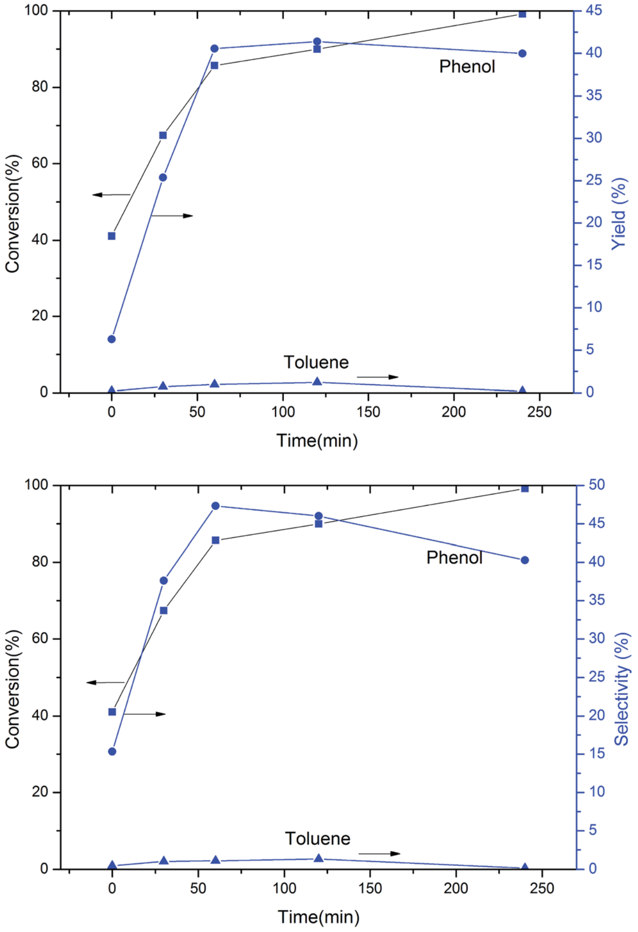

Fig. 4 Product yield and selectivity of benzyl phenyl ether at different reaction time. Reaction conditions: 0.2 g benzyl phenyl ether, 0.1 g ZrP and 0.1 g Pd/C, 15 mL H_2O, 200 °C.

and/or benzyl alcohol under microwave heating are shown in Table 3.

With phenol as the reactant and ZrP as the catalyst, 97.20% phenol was recovered, and no other products were detected by GC. When Pd/C or ZrP–Pd/C were used as the catalyst, the unreacted amount of phenol was high as well (91.28–91.91%). The results indicate that phenol is very stable even with the catalyst present.

Table 3 Product yields and selectivity of phenol and/or benzyl alcohol under microwave heating

Reactant	Catalyst	Phenol (%)	Benzyl alcohol (%)
Phenol	ZrP	97.2[a]	0.00[a]
Phenol	Pd/C	91.28[a]	0.00[a]
Phenol	ZrP–Pd/C	91.91[a]	0.00[a]
Benzyl alcohol	ZrP	4.50[b]	95.56[b]
Benzyl alcohol	Pd/C	1.77[b]	0.00[b]
Benzyl alcohol	ZrP–Pd/C	0.67[b]	0.00[b]
Benzyl alcohol + phenol	ZrP	101.83[a]	96.29[b]
Benzyl alcohol + phenol	Pd/C	109.53[a]	12.24[b]
Benzyl alcohol + phenol	ZrP–Pd/C	112.31[a]	4.17[b]

[a] Calculated based on the mass amount of initial phenol. [b] Calculated based on the mass amount of initial benzyl alcohol. Reaction conditions: 0.2 g benzyl phenyl ether, 0.1 g ZrP and 0.1 g Pd/C, 15 mL H_2O, 200 °C.

When benzyl alcohol was used as the reactant, 95.56% benzyl alcohol remained after 1 h with ZrP as the catalyst, and 4.50% phenol was formed. This shows that benzyl alcohol is also relatively stable over ZrP. Treated with Pd/C or ZrP–Pd/C as the catalyst, only 1.77% and 0.67% phenol was produced, respectively. However, it is interesting that no unreacted benzyl alcohol or any other products was identified, showing that benzyl alcohol has all been consumed.

When phenol and benzyl alcohol were used as the reactants and ZrP used as the catalyst, the amount of phenol increased slightly, and the amount of benzyl alcohol decreased slightly to 96.29%. This is consistent with the result using phenol and benzyl alcohol as the reactant respectively. With Pd/C or ZrP–Pd/C as the catalyst, the amount of phenol increased slightly, while the amount of benzyl alcohol decreased greatly to 12.24% and 4.17% respectively, which is also consistent with the reaction using benzyl alcohol as the reactant. Therefore, it could be proposed that catalyzed by Pd/C, benzyl alcohol formed by the depolymerization of benzyl phenyl ether would undergo some further reaction forming products which could not be identified by GC, such as oligomers. If such repolymerization could be inhibited, the total yield of monomeric aromatics would be improved greatly.

3.7. Summary of the depolymerization mechanism of BPE

Various reaction mechanism has been proposed for the depolymerization of benzyl phenyl ether. One proposed mechanism was that in supercritical water, the cleavage of α-O-4 bond was proceeded *via* parallel hydrolysis and pyrolysis pathways to form phenol and toluene.[35] Siskin *et al.* proposed that the radical pathway dominated the reaction above 350 °C in the aqueous phase, while at the temperature lower than 250 °C the ionic chemistry was the main pathway.[36] He *et al.* also proposed that the C–O cleavage of benzyl phenyl ether proceeded along an ionic pathway rather than a thermal/free-radical route at 250 °C.[21] Because of the presence of H_2, only a slight amount of alkylation products were found in their work. Roberts *et al.* proposed that in the presence of alkali carbonate, the metal ion led to the formation of a cation-benzyl phenyl ether adduct, in which the ether bond was polarized and prone to be heterolytically cleaved.[19]

Based on the previous results, possible catalyzed reaction pathway of benzyl phenyl ether was shown in Fig. 5. It could be proposed that in our case treated with ZrP, benzyl phenyl ether will firstly be hydrolyzed forming phenol and benzyl alcohol. Slight amount of benzyl alcohol will react further, resulting in the relatively lower yield of benzyl alcohol than phenol.

For the circumstance of Pd/C, benzyl phenyl ether will be depolymerized first forming phenol and benzyl alcohol. One possible pathway is that ether bond in benzyl phenyl ether will be polarized by forming the metal-benzyl phenyl ether, and thus was easily to be heterolytically cleaved.[19] The benzyl alcohol will undergone further alkylation reaction forming undetected oligomer products.

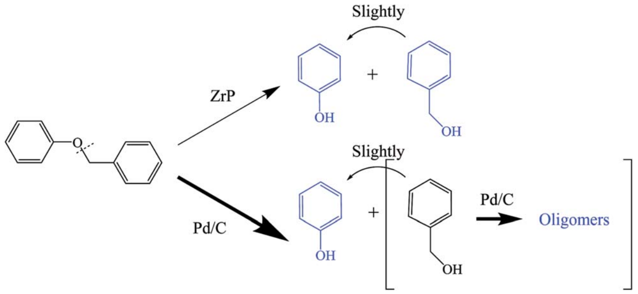

Fig. 5 Possible reaction pathway for the cleavage of benzyl phenyl ether in presence of ZrP and Pd/C.

In the presence of ZrP–Pd/C mixture catalysts, both catalysts contribute to the depolymerization. While the benzyl alcohol formed by the catalysis ZrP will be catalyzed again by Pd/C forming alkylation products.

4. Conclusion

The yield of phenol increased effectively in the presence of ZrP or SBA-15 doped with metal catalyst (Pd/C or Ru/C), and 40.55% phenol was produced over ZrP–Pd/C. As the main primary products, phenol was stable, while benzyl alcohol reacted easily forming oligomers over Pd. It is proposed that under the catalysis of ZrP–Pd/C hybrid catalyst, benzyl phenyl ether will firstly be decomposed into phenol and benzyl alcohol, and benzyl alcohol will then undergo repolymerization forming polymers.

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