Journal of Catalysis 311 (2014) 41-51

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Mechanisms of catalytic cleavage of benzyl phenyl ether in aqueous and apolar phases



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ARTICLE INFO

Article history: Received 9 August 2013 Revised 28 October 2013 Accepted 30 October 2013

Keywords: Lignin Hydrolysis Hydrogenolysis Ether cleavage Alkylation Pyrolysis

ABSTRACT

Catalytic pathways for the cleavage of ether bonds in benzyl phenyl ether (BPE) in liquid phase using Ni- and zeolite-based catalysts are explored. In the absence of catalysts, the C–O bond is selectively cleaved in water by hydrolysis, forming phenol and benzyl alcohol as intermediates, followed by alkylation. The hydronium ions catalyzing the reactions are provided by the dissociation of water at 523 K. Upon addition of HZSM-5, rates of hydrolysis and alkylation are markedly increased in relation to proton concentrations. In the presence of Ni/SiO₂, the selective hydrogenolysis dominates for cleaving the C_{aliphatic}–O bond. Catalyzed by the dual-functional Ni/HZSM-5, hydrogenolysis occurs as the major route rather than hydrolysis (minor route). In apolar undecane, the non-catalytic thermal pyrolysis route dominates. Hydrogenolysis of BPE appears to be the major reaction pathway in undecane in the presence of Ni/SiO₂ or Ni/HZSM-5, almost completely suppressing radical reactions. Density functional theory (DFT) calculations strongly support the proposed C–O bond cleavage mechanisms on BPE in aqueous and apolar phases. These calculations show that BPE is initially protonated and subsequently hydrolyzed in the aqueous phase. DFT calculations suggest that the radical reactions in non-polar solvents lead to primary benzyl and phenoxy radicals in undecane, which leads to heavier condensation products as long as metals are absent for providing dissociated hydrogen.

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1. Introduction

Lignin is a three-dimensional amorphous polymer with methoxylated phenyl-propane units, which are randomly connected by C–O or C–C linkages [1]. It would be ideal to catalytically and efficiently convert lignin to liquid transportation fuels or fine chemicals without destroying its inherent benzene structure. However, currently lignin is primarily used as a low-grade fuel to provide heat [2,3].Three major approaches, i.e., gasification of lignin to synthesis gas [4,5], liquefaction (pyrolysis) of lignin to bio-oil [6,7], and hydrolysis of lignin to monomeric or oligomeric units [8–10], are used to depolymerize lignin. As the hydrolysis route leads to relatively selective products under much milder reaction conditions, it is rational to select lignin model compounds such as aryl ether dimers to investigate the principal fundamental chemistry of the hydrothermal depolymerization of lignin. The most abundant C–O bonds in lignin are α -O-4, β -O-4, 4-O-5, β -1, and 5–5 linkages [11], in which the α -O-4 bond is the most active and thermally unstable one due to the lowest bond dissociation energy of the aliphatic C–O bond (218 kJ mol⁻¹) among these bonds [12–15]. To explore the mechanism of cleaving the α -O-4 bond, BPE has been selected as the model compound in this work.

The non-catalyzed pyrolysis of BPE has been extensively investigated in the past [16]. It is initiated by homolytic scission of the weak Caliphatic-O bond above 548 K. Generally, pyrolysis was, however, carried out under more severe conditions above 593 K in the vapor phase or in supercritical solvents such as methanol [17], toluene [18], and tetralin [18]. The pyrolysis process produces high concentrations of benzyl and phenoxy radicals, which led to toluene and phenol formation as primary products, together with dimer and high molecular weight products derived from the recombination of the initial radicals. The recombination yield was usually higher than 15% with a carbon balance lower than 80%. Water, in contrast, leads to higher hydrothermal conversion rates of BPE than neat pyrolysis. Klein et al. [19] reported that the pyrolysis rate of BPE in the presence of water was approximately four times higher than that in neat pyrolysis at 605 K. We have explored BPE conversion in supercritical water (between 543 K and 623 K) as well via analyzing the influence of salts (alkali carbonates) toward BPE conversion in aqueous phase [20].





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^{0021-9517/\$ -} see front matter © 2013 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcat.2013.10.024

Recently, we have reported that diverse lignin-derived aryl ethers can be cleaved with Ni/HZSM-5 or Ni/SiO₂ at 393–523 K via combined hydrogenolysis, hydrolysis, and hydrodeoxygenation integrated steps in the aqueous phase [21–24]; however, the mechanisms for cleaving of C–O bonds in these ethers have not been unequivocally established in the presence of mono- and dual-functional metal and acid catalysts. In this work, we will, therefore, investigate the roles of gas atmosphere, acid and metal sites, as well as their cooperative action in the conversion of BPE in the aqueous phase at 523 K via exploring the detailed kinetics together with the analysis of reaction pathways and mechanisms for BPE conversion at specifically varied conditions. In addition, density functional theory (DFT) modeling is comparatively employed to explore the ether cleavage mechanisms in the aqueous and apolar phases as well.

2. Experimental section

2.1. Chemicals

The chemicals were purchased from commercial suppliers and used as received: benzyl phenyl ether (TCI, >98% GC assay), nickel(II) nitrate hexahydrate (Sigma–Aldrich, \geq 98.5% GC assay), SiO₂ (Aerosil 200, Evonik-Degussa), HZSM-5 (Clariant AG, Si/Al = 45), Ni/SiO₂ (Acros, Ni loading 70%), H₂SO₄ (ROTH, \geq 95.5%), undecane (Sigma–Aldrich, >99% GC assay), H₂ (Westfalen AG, >99.999 vol.%), N₂ (Westfalen AG, >99.999 vol.%), synthetic air (Westfalen AG, >99.999 vol.%), and water (EASYpure II, resistivity:18.2 M Ω cm).

2.2. Preparation of Ni/HZSM-5

Ni/HZSM-5 catalyst was synthesized by the wetness impregnation method as follows, Ni(NO₃)₂·6H₂O (5.6 g) was first dissolved in H₂O (5.0 g) as a transparent green solution, and subsequently, such aqueous solution was slowly dropped into zeolite HZSM-5 powder (10 g) with stirring. After metal incorporation for 2 h, the catalyst was sequentially dried at 373 K for 12 h, air-calcined (flow rate: 100 mL min⁻¹) at 673 K for 4 h, and hydrogen-reduced (flow rate: 100 mL min⁻¹) at 733 K for 4 h.

2.3. Catalyst characterization

Atomic absorption spectroscopy (AAS): A UNICAM 939 AAspectrometer was used to measure the Ni concentrations of Ni/SiO₂ and Ni/HZSM-5.

BET surface area: The surface areas and pore diameters were determined by the nitrogen sorption measurement. A PMI automated BET sorptometer was used to measure the nitrogen adsorption at 77 K and before measurement, the samples were first outgassed at 523 K for 20 h.

 H_2 chemisorption: The catalysts were first activated at 733 K for 3 h in H_2 and 1 h in vacuum and then cooled to 313 K. An isotherm of H_2 adsorption (chemisorption and physisorption) was measured within a pressure range from 1 kPa to 40 kPa. Then, the physisorbed H_2 was removed by outgassing the sample at the same temperature for 1 h, and another adsorption isotherm (physisorption) was taken. The concentration of chemisorbed H_2 on the metal was determined by extrapolating the differential isotherm to zero P_{H2} , and this value was used to calculate the dispersion of Ni with the assumption of H:Ni atomic ratio = 1.

Transmission electron microscopy (TEM): A JEM-2010 JEOL transmission electron microscope operating at 120 kV was used to record the TEM images. Before measurement, the catalyst was ground and then suspended in ethanol and subsequently dispersed

by ultrasonic treatment. After that, the dispersion was dropped on a copper grid-supported carbon film.

IR spectra of adsorbed pyridine: IR spectroscopy with pyridine as probe molecule was used to determine the acid site concentrations and distributions. The IR spectra were measured with a PerkinElmer 2000 spectrometer operated at a resolution of 4 cm⁻¹. The sample was activated at 723 K for 2 h in vacuum, and a background spectrum was recorded after the temperature decreased to 423 K. The activated sample was exposed to pyridine vapor $(1.0 \times 10^{-5} \text{ MPa})$ at 423 K for 0.5 h. After removing physisorbed pyridine by outgassing at 423 K for 0.5 h, the spectra were recorded. For quantification, molar integral extinction coefficients of 0.73 cm µmol⁻¹ and 0.96 cm µmol⁻¹ were used for Brønsted (BAS) and Lewis acid sites (LAS), respectively.

2.4. Catalytic test

The detailed reaction conditions are described in the corresponding figures as footnotes. In a typical experiment, the catalytic reactions were carried out in a slurry autoclave reactor loaded with Ni/HZSM-5 in the water solvent at 523 K in the presence of 4 MPa H₂ (STP). A mixture of benzyl phenyl ether (0.010 mol), 10 wt.% Ni/ HZSM-5 (0.050 g, 8.62×10^{-5} mol Ni), and H₂O (80 mL) was firstly added into a Parr reactor (Series 4848, 300 mL). After the reactor was flushed with H₂ by three times, the autoclave was charged with 4 MPa H₂ (ambient temperature) and the reaction was conducted at 523 K with a stirring speed of 700 rpm at different reaction times. The temperature of the autoclave was increased in approximately 20 min. from ambient to reaction temperature (523 K). Because it is a two-phase reaction, the kinetics data are collected at different duration times. After reaction, the reactor was cooled by ice to ambient temperature, and the organic products were extracted by ethyl acetate and analyzed by GC and MS. The products were analyzed by a gas chromatography (GC) and GC-mass spectroscopy (GC-MS) on Shimadzu 2010 gas chromatograph with flame ionization detector and a Shimadzu QP 2010S GC–MS, both of them equipped with a HP-5 capillary column $(30 \text{ m} \times 250 \text{ }\mu\text{m})$. Internal standard, i.e., 2-isopropylphenol, was used to determine the liquid product concentration and carbon balance. The carbon balance for all reported experiments in liquid phase was better than 95 ± 3% in this work. The calculations of conversion and selectivity were based on carbon mole basis. Conversion = (the amount of raw materials change during reaction/total amount of raw materials) \times 100%. Selectivity = (C atoms in each product/total C atoms in the products) \times 100%. Rate = (moles of reactants cleaved)/(reaction time in hour). TOF = (moles of reactants cleaved)/(moles of surface active sites × reaction time in hour).

2.5. Density functional theory (DFT) calculation

All the quantum chemical calculations of BPE in hot water and undecane were performed using Gaussian 09 program [25]. The DFT/B3LYP functional with 6-311++G(d,p) basis set was applied. The accuracy of the B3LYP functional was checked by comparing with the second-order Möller–Plesset perturbation theory (MP2) [26]. The transition state of each reaction pathway is located using the linear (LST) and quadratic synchronous transit (QST) methods [27,28]. A series of single point energy calculations of interpolated structures between the initial and the final states along the reaction pathway are performed. The maximum energy structure along this reaction path is used as an estimate transition state in the QST calculation. Each identified transition state was confirmed by the sole imaginary vibrational frequency. The solvation effects on the hydrolysis in water and the pyrolysis in undecane were described by the polarizable continuum model (PCM) model with dielectric constants of 78.3553 for water and 1.9910 for undecane [29].

3. Results and discussion

3.1. Catalysts characterization

The physicochemical properties of the supported metal catalyst (Ni/SiO₂), the acid catalyst (HZSM-5), and the dual-functional catalyst (Ni/HZSM-5) are compiled in Table 1. The Ni/SiO₂ catalyst had a Ni content of 70 wt.%, a BET-specific surface area of 82 m² g⁻¹, pore volume of 0.12 $\mbox{cm}^3\,\mbox{g}^{-1}$, and a pore diameter of 9.2 nm. The average size of supported Ni particles in Ni/SiO₂ was around 8.0 nm determined from the TEM image (Supporting information Fig. S1b). The parent HZSM-5 had a BET surface area of $395 \text{ m}^2 \text{g}^{-1}$ and a total acid site concentration of 0.360 mmol g⁻¹ determined by TPD of ammonia (TPD-NH₃). Probed by IR of adsorbed pyridine (Py-IR), the Brønsted acid site (BAS) and Lewis acid site (LAS) concentration of HZSM-5 was 0.266 and 0.048 mmol g^{-1} , respectively. Impregnated with Ni, the BET surface of Ni/HZSM-5 (Ni content: 10 wt.%) decreased to $374 \text{ m}^2 \text{ g}^{-1}$. The concentration of the Brønsted acid sites decreased by approximately 20% after Ni incorporation due to the ion exchange of Brønsted acid sites for Ni²⁺, while the Lewis acid site concentration was almost unchanged compared to parent zeolite. The average Ni particle size was 20 nm on Ni/HZSM-5 prepared by impregnation as determined by the TEM image (Supporting information Fig. S1a).

3.2. Benzyl phenyl ether conversion in the aqueous phase

High-temperature water has a density and polarity at 573 K similar to acetone at ambient temperature [30] and acts consequently as a suitable reaction medium for dissolving organic compounds. The dielectric constant of water drops rapidly from 78 at 293 K to 27 at 523 K, and the ionic product of water is 10^{-11} at 523 K compared to 10^{-14} at 293 K [31,32]. This indicates that the high-temperature water could act as a moderately strong acid as well as a base. We structure the investigations of the influence of gas atmosphere, of a solid acid introduced in the form of HZSM-5, of metal sites introduced by Ni/SiO₂, and the presence of both sites by introducing Ni/HZSM-5, on BPE conversion at 523 K in four sections, i.e., (i) BPE conversion in aqueous phase in the absence and the presence of H₂, (ii) the influence of acid on BPE conversion in aqueous phase in the presence of H₂, (iii) the influence of metal on BPE conversion in the presence of H₂, (iv) the influence of bifunctionality with acid and metal sites on BPE conversion in the presence of H_2 .

3.2.1. BPE conversion in aqueous phase in the absence and the presence of $\rm H_2$

Fig. 1a shows that BPE was equally cleaved into phenol (Ph) and benzyl alcohol (BA) in water at 523 K in the absence of H_2

(0.1 MPa N ₂). Without catalyst, hydronium ions from dissociat	ted
water at 523 K (pH = 5.5) catalyze the hydrolysis $[31,32]$. At the	se-
lected conditions, the conversion increased linearly to 31% a	s a
function of time up to 110 min, and the yields of phenol and ben	zvl
alcohol synchronously increased to around 13%. Besides Ph and	BA.
some products with 13 C atoms such as 4-benzyl phenol and	2-
benzyl phenol were also observed. It was reported that these h	- еа-
vier products were dimers or trimers formed from BPF pyrolysis	cu cor
hydrolysis via recombination of radical intermediates [203	231
However Siskip et al. proposed a different mechanism on RDE of	ן כי מים
version at different temperature ranges is above 622 K the r	on-
version at uniferent temperature failges, i.e., above 025 K, the fa	au- the
ical pathway dominated, but at the lower temperature 525 K in	the
aqueous phase, the contribution of the ionic chemistry was co	- nc
cluded to play a significant role [34]. Siskin et al., nowever, also d	DD-
served the formation of phenol (41.0%), benzyl alcohol (26.4%), a	ind
alkylated products (29.6%, including 19.6% dimers and 10% trime	ers)
at 523 K. The higher yield of alkylated products, especially of	tri-
mers in their case, is attributed to the much longer reaction ti	me
(5.5 days) than the 110 min in our case. In our work, the yield	of
the C-C coupled products continuously increased to 5% af	ter
achieving the specific reaction equilibrium. When the gas atn	no-
sphere was altered to H ₂ (Fig. 1c), 34% conversion was attain	ıed
in 110 min, which was close to the conversion obtained in t	the
presence of 0.1 MPa N ₂ . The major products of Ph and BA w	ere
formed via hydrolysis by hydronium in the high-temperate	ure
water, and the C–C alkylation products kept a stable yield of	5%.
This indicates that gas atmosphere ($P = 0.1$ MPa) exerts a negligi	ble
influence to the hydrolysis of BPE in the aqueous phase.	

With high-pressure N₂ (4 MPa, Fig. 1b), however, the hydrolysis rates were significantly accelerated with a high conversion of 41% in 110 min. At a high H₂ pressure (4 MPa) under hydrothermal conditions, the cleavage rates on BPE were further enhanced leading to 51% conversion in 110 min. (Fig. 1d); equal concentrations (23%) of phenol and benzyl alcohol were formed. In addition, the C-C coupling products also attained a maximum yield of 5% in water, and this constancy implied that the C-C coupling is primarily dominated by the acid-catalyzed alkylation, but not by the thermal free-radical reaction [35]. Summarizing these results leads to the conclusion that the aqueous environment favors the ionic pathway in the C-O bond cleavage of BPE at 523 K. BPE is then cleaved to phenol and benzyl alcohol by hydrolysis, which is catalyzed by the protons of high-temperature water in the absence or the presence of H₂. The subsequent alkylation between phenol and alcohol reaches a maximum yield of 5%.

The relationship between the hydrolysis rate and the gas pressure in the aqueous phase has been systematically investigated by Whalley et al. It has been shown that in the ether hydrolysis based on A2 mechanism (with the rate-determining step being the bimolecular hydrolysis), the higher gas pressure enhances the ether hydrolysis rate in the aqueous phase due to a better stabilization of the transition state via the increased gas pressure [36,37]. The A2 mechanism of hydrolysis of BPE is described in equations 1–4. In agreement with Whalley et al.

Table 1			
Physicochemical	properties	of	catalysts.

NI: /0: 0		
N1/S1O ₂	HZSM-5 (SI/AI = 45)	N1/HZSM-5(S1/AI = 45)
70	-	10
82	395	374
0.12	0.26	0.24
9.2	3.6	3.6
8.0	-	20
-	0.360	0.296
-	0.266	0.228
-	0.048	0.048
6.9	-	0.84
	70 82 0.12 9.2 8.0 - - - 6.9	70 - 82 395 0.12 0.26 9.2 3.6 8.0 - - 0.360 - 0.266 - 0.266 - 0.048 6.9 -



Fig. 1. Product yields for conversion of benzyl phenyl ether in aqueous phase in the absence and the presence of H₂ as a function of time. Reaction conditions: benzyl phenyl ether (1.84 g), H₂O (80 mL), 523 K, stirring at 700 rpm, (a) 0.1 MPa N₂, (b) 4 MPa N₂, (c) 0.1 MPa H₂, (d) 4 MPa H₂.

[37], our results also show that the TOF of BPE hydrolysis increased from $7.6\times10^3\,mol\,mol_{[H^+]H_20}^{-1}\,h^{-1}$ at 0.1 MPa H_2 to $1.1\times10^4\,mol\,mol_{[H^+]H_20}^{-1}\,h^{-1}$ at 4 MPa H_2 .

$$H^+$$
 + H_2O \longrightarrow H_3O^+ (1)

$$\begin{array}{c} C_{6}H_{5} \\ \hline \\ C_{7}H_{7} \end{array} O + H_{3}O^{+} \end{array} \xrightarrow{C_{6}H_{5}} OH^{*} + H_{2}O$$

$$(2)$$

$$C_6H_5$$

 C_7H_7 OH⁺ + H₂O \longrightarrow C₇H₇OH + C₆H₅O⁺H₂
(3)

$$C_6H_5O^+H_2 + H_2O \xrightarrow{fast} C_6H_5OH + H_3O^+$$
(4)

The higher C–O cleavage rate of BPE in H_2 compared to N_2 with a pressure of 4 MPa may be originated from the different solubilities of the gases in the aqueous phase. When a reaction takes place in solvents, the reactant is surrounded by solvent molecules and needs to overcome the cage of solvents to collide with reactants or catalysts. This is called "cage effect." We speculate that the higher solubility of H_2 compared to N_2 leads to a lower equilibrium pressure and, hence, less compression and a more loose solvent cage for the reactant, facilitating reaction from the solvent cage, enhancing in turn the reaction rate with H_2 in comparison with N_2 . At present, however, we cannot fully exclude a direct positive effect of the H_2 pressure on the acid-catalyzed reactions.

3.2.2. The influence of acid on BPE conversion in the aqueous phase in the presence of H_2

The impact of the acid after loading low (0.03 g) and high (0.15 g) concentrations of HZSM-5 was subsequently investigated at 523 K in the conversion of BPE at 4 MPa H₂ (Fig. 2a and b). With a small concentration of HZSM-5 (0.03 g), the conversion was increased from 51% to 75% compared to in the neat aqueous phase with 4.0 MPa H₂ in 110 min (Fig. 2a). Meanwhile, the cleavage yields to phenol and benzyl alcohol (30%) were comparable to those (23%) in the absence of acid. But it is interesting to find that the small addition of the acid remarkably enhanced the alkylation yield from 5% to 15% at 523 K. It supports again that C_{13} products are formed by acid-catalyzed alkylation and not by free-radical reactions.

In a comparison, with a high concentration of solid acid (HZSM-5, 0.15 g), the conversion increased to 87% in the first 10 min, and further increased to 98% at 110 min, which was much higher than the conversion (only 51%) without introducing the HZSM-5 at identical conditions (Fig. 2b). This confirms that hydrolysis is indeed the major reaction pathway for BPE conversion in aqueous phase. It should be emphasized that the alkylation yield reached 50% under these conditions, which is much higher than that in neat



Fig. 2. Product yields for conversion of benzyl phenyl ether with HZSM-5 in aqueous phase in the presence of H₂ as a function of time. Reaction conditions: benzyl phenyl ether (1.84 g), H₂O (80 mL), 523 K, 4 MPa H₂, stirring at 700 rpm, (a) HZSM-5 (0.03 g), (b) HZSM-5 (0.15 g).

water with or without hydrogen (5%), or with small concentrations of HZSM-5 (15%). This indicates that with a sufficient concentration of acid sites, the initial hydrolysis and following alkylation rates are both highly accelerated.

With the addition of HZSM-5, the major pathway was still hydrolysis for BPE in water at 523 K. The rate of hydrolysis and following alkylation between the intermediate fragments were both enhanced with a small concentration of HZSM-5. Adding a higher concentration of acid sites (higher amount of HZSM-5 added) promoted both the hydrolysis and alkylation rates to a larger extent.

3.2.3. The influence of metal on aqueous-phase BPE conversion in the presence of H_2

The metal site (Ni/SiO₂) expectedly catalyzed a different pathway of BPE conversion in water at 523 K (see Fig. 3). After 110 min, BPE was quantitatively cleaved to 50% phenol and 50% toluene. This suggests that the weaker $C_{aliphatic}$ –O bond (bond dissociation energy: 218 kJ mol⁻¹) [14] is selectively cleaved by Ni-catalyzed hydrogenolysis, but not by acid-catalyzed hydrolysis. Note that the alternative products (benzene and benzyl alcohol) by



Fig. 3. Product yields for conversion of benzyl phenyl ether with Ni/SiO_2 in aqueous phase in the presence of H_2 as a function of time. Reaction conditions: benzyl phenyl ether (9.20 g), Ni/SiO_2 (70 wt.%, 0.010 g), H_2O (80 mL), 523 K, 4 MPa H_2 , stirring at 700 rpm.

cleaving of the other side of $C_{aromatic}$ –O bond (bond dissociation energy: 314 kJ mol⁻¹) [14] were not observed. Five percentage of alkylation products (catalyzed by hydronium ions formed by dissociated water at 523 K) were formed as well, indicating that the hydrolysis/alkylation route contributes to a very minor part. The alkylation yield was quite constant at 5% without the acid, as the pH value in such aqueous system is stable at 5.5 [31,32].

The observed yield of phenol was much lower than the yield of toluene, as the hydrogenation rate of phenol ($2400 h^{-1}$) was much faster than the hydrogenation rate of toluene on Ni/SiO₂ ($135 h^{-1}$) at 523 K. (Supporting information Table S1). After phenol was hydrogenated to cyclohexanone and cyclohexanol on Ni, cyclohexanol was subsequently dehydrated to cyclohexene catalyzed by hydronium ions and then hydrogenated or dehydrogenated to cyclohexane or benzene, respectively. However, all these hydrodeoxygenated intermediates from phenol were detected with yields lower than 7% (not shown in Fig. 3).

In summary, the Ni-catalyzed direct hydrogenolysis on BPE is the dominating pathway for producing equal concentrations of phenol and toluene. Subsequently, phenol was hydrogenated at a relatively fast rate, forming cyclohexanone and cyclohexanol as intermediates. In turn these, oxygenates were deoxygenated to cyclohexene, cyclohexane, and benzene catalyzed by the joint action of metal (Ni/SiO₂) and acid (hydronium ions in the hightemperature water).

3.2.4. The influence of bifunctionality with acid and metal sites on aqueous-phase BPE conversion in the presence of H_2

The role of acid and metal sites in proximity on Ni/HZSM-5 was investigated in the next step. Fig. 4 shows the variations in the concentration in the reactant product mixture of BPE over Ni/HZSM-5 as a function of time. The products included 50% phenol, 40% toluene, 2% benzyl alcohol, as well as 8% C13 alkylated products, with quantitative conversion after 240 min. With metal and acid sites in Ni/HZSM-5, phenol and toluene (major products) were produced by metal-catalyzed hydrogenolysis, while the parallel acidcatalyzed hydrolysis (minor) pathway led to the formation of phenol and benzyl alcohol as well as some alkylation products. The hydrolysis was catalyzed by the acid sites of Ni/HZSM-5 and protons in high-temperature water, attaining a maximum alkylation yield of 10%. It is noted that the turnover frequencies of protons/hydronium ions in the zeolite channels (Table 2, Entry 4-6) were approximately one magnitude lower than those of water dissociation. The hydrogenolysis rate was at least four times as fast



Fig. 4. Product yields for conversion of benzyl phenyl ether with 10% Ni/HZSM-5 in aqueous phase in the presence of H_2 as a function of time. Reaction conditions: benzyl phenyl ether (9.20 g), 10 wt.% Ni/HZSM-5 (0.050 g), H_2O (80 mL), 523 K, 4 MPa H_2 , stirring at 700 rpm.

as that of hydrolysis, as the yield of the hydrogenolyzed products (80%) was much higher than that of hydrolyzed (20%). Trace amounts (yields < 2%) of hydrodeoxygenation intermediates from phenol and toluene such as cyclohexanone, cyclohexanol, and methylcyclohexane were observed as well (not shown in Fig. 4).

With both catalytic sites present, the hydrogenolysis route catalyzed by metallic Ni was the major reaction pathway for cleaving the C–O bond of BPE, with producing phenol and toluene as major products. Hydrolysis was only the minor route, but hydrodeoxygenation of phenol and toluene occurred to a small extent with Ni/HZSM-5 as well. Alkylation of the cleaved products (phenol and benzyl alcohol) took place with HZSM-5 catalyst in the hightemperature water. 3.3. Different mechanisms for cleaving of the C-O bond of BPE at varying conditions in aqueous phase

The variations in product distributions and reaction rates on the varying conditions in the aqueous phase are compiled in Table 2. In N_2 (*P* = 0.1 MPa), BPE was cleaved into phenol and benzyl alcohol by hydrolysis under the hydrothermal conditions with an initial cleavage rate of 0.0017 mol h^{-1} and a TOF of 6.8×10^3 mol mol_{[H⁺|H₂0</sup> h^{-1} ; 5% of alkylation products were} formed at such conditions (Table 2, Entry 1). Replacing N_2 by H_2 (P = 0.1 MPa), the C–O bond cleavage rate (0.0019 mol h⁻¹) and TOF $(7.6 \times 10^3 \text{ mol mol}_{[\text{H}^+]\text{H}_20}^{-1} \text{ h}^{-1})$ (Table 2, Entry 3) were comparable to these reactions in 0.1 MPa N₂ (0.0017 mol h⁻¹ and $6.8 \times 10^3 \text{ mol mol}_{[\text{H}^+]\text{H}_20}^{-1} \text{ h}^{-1}$). This implies that gas atmosphere does very minor impact to the ether hydrolysis rate at a pressure of 0.1 MPa. Employing a high-pressure in the presence of N₂ (4.0 MPa), the reaction rate was accelerated leading to a conversion of 41%, with an increased initial cleavage rate of 0.0022 mol h^{-1} and TOF of $8.8\times10^3\,mol\,mol_{[H^+]H_20}^{-1}\,h^{-1}$ (Table 2, Entry 2). With 4.0 MPa H₂, 51% conversion was reached under identical conditions with an increased initial cleavage rate of 0.0028 mol h⁻¹ and TOF of 1.1×10^4 mol mol⁻¹_{[H⁺]H₂0} h⁻¹ (Table 2, Entry 4). The yield of alkylation was maintained at the stable level of around 5% in the aqueous phase in the presence of H₂ or N₂, suggesting the alkylation equilibrium exists [35].

The addition of even a small amount of acid (HZSM-5, 0.030 g) increased the cleavage rate of BPE threefold in the presence of H₂, i.e., it attains an initial cleavage rate of 0.0090 mol h⁻¹ compared to 0.0028 mol h⁻¹ without the solid acid (Table 2, Entry 5). Yields of hydrolysis and alkylation were increased by 5–10% in 110 min. Employing a higher concentration of acid (HZSM-5, 0.15 g), the initial TOF $(1.3 \times 10^3 \text{ mol mol}_{[\text{H}^+]\text{HZSM-5}}^{-1} \text{h}^{-1})$ (Table 2, Entry 6) was comparable to that with a small amount of acid $(1.1 \times 10^3 \text{ mol mol}_{[\text{H}^+]\text{HZSM-5}}^{-1} \text{h}^{-1})$. However, the reaction rate was higher and the reaction reached full conversion with equal yields of hydrolysis (50%) and alkylation products (50%) in 110 min

Table 2

The effect of gas atmosphere, HZSM-5 (acid), and Ni/SiO₂ (metal) on the reaction of BPE in the aqueous phase at 523 K.^a

Entry	Gas	Active site	Rate (mol h^{-1})	TOF (mol mol ^{-1} h ^{-1})
1 ^b	N ₂ ^c	H ₂ O	0.0017	$6.8 \times 10^3 \text{ mol mol}_{\text{IH}^+\text{IH}_{*}\text{O}}^{-1} \text{ h}^{-1}$
		$n ([\mathrm{H^+}]_{\mathrm{H_2O}}) = 2.5 \times 10^{-7} \mathrm{mol}$		[n]n20
2 ^b	N ₂	H ₂ O	0.0022	$8.8 imes 10^3 \text{ mol mol}_{[\text{H}^+]\text{H}_2\text{O}}^{-1} \text{ h}^{-1}$
- b		$n ([\mathrm{H^+}]_{\mathrm{H_2O}}) = 2.5 \times 10^{-7} \mathrm{mol}$		
30	H ₂ ^c	H_2O	0.0019	$7.6\times 10^3\ mol\ mol_{[H^+]H_2O}^{-1}\ h^{-1}$
٨b		$n([H^+]_{H_2O}) = 2.5 \times 10^{-7} \text{ mol}$	0.0000	
45	H ₂	H_2U	0.0028	$1.1 \times 10^4 \text{ mol mol}_{[\text{H}^+]\text{H}_2\text{O}}^{-1} \text{ h}^{-1}$
- b	п	$H([\Pi]_{H_{2}O}) = 2.3 \times 10^{-110}$	0.0000	
J	112	$n([H^+]_{UZME}) = 8.0 \times 10^{-6} \text{ mol}$	0.0090	$1.1 \times 10^{3} \text{ mol mol}_{[\text{H}^+]\text{HZSM-5}} \text{ h}^{-1}$
		$n([H^+]_{H,0}) = 2.5 \times 10^{-7} \text{ mol}$		
6 ^b	H ₂	HZSM-5, H ₂ O	0.0522	1.3×10^3 mol mol ⁻¹
		$n ([H^+]_{HZSM-5}) = 4.0 \times 10^{-5} \text{ mol}$		
		$n ([\mathrm{H^+}]_{\mathrm{H_2O}}) = 2.5 \times 10^{-7} \mathrm{mol}$		
7 ^d	H ₂	H_2SO_4 , H_2O	0.0542	$1.4 imes 10^3 mol mol_{[{ m H}^+]}^{-1} h^{-1}$
		$n ([\mathrm{H^+}]_{\mathrm{H_2SO_4}}) = 4.0 \times 10^{-5} \mathrm{mol}$		1 3
		$n ([\mathrm{H^+}]_{\mathrm{H_2O}}) = 2.5 \times 10^{-7} \mathrm{mol}$		
8 ^b	H ₂	70 wt.% Ni/SiO ₂ , H ₂ O	0.1410	$1.7 imes 10^4~mol~mol_{Surf~Ni}^{-1}~h^{-1}$
- b		n ([Surf. Ni]) = 8.5 × 10 ⁻⁶ mol, n ([H ⁺] _{H₂0}) = 2.5 × 10 ⁻⁷ mol		
9 ⁶	H ₂	10 wt.% Ni/HZSM-5, H ₂ O	0.0777	$1.1 \times 10^5 \text{ mol mol}_{Surf Ni}^{-1} \text{ h}^{-1}$
		$n ([Surf. NI]) = 7.4 \times 10^{-5} \text{ mol}$ $n ([H^+]_{views, r}) = 1.0 \times 10^{-5} \text{ mol}$		
		$n ([H^+]_{H2SM-5}) = 1.0 \times 10^{-10} \text{ mol}$		
		H_{20}		

^a Gas pressure: 4.0 MPa.

^b The initial rate and TOF are obtained via the kinetics in the aqueous phase in Figs. 1–4.

^c Gas pressure: 0.1 MPa.

^d Rate and TOF are calculated based on the data listed in Supporting information Table S2.



Fig. 5. Arrhenius plots for the ln TOF (h⁻¹) with H_2SO_4 and HZSM-5 catalysts in the temperature range of 483–543 K in the presence of 4 MPa H₂. Reaction conditions: benzyl phenyl ether (18.4 g), H_2SO_4 solution ($c = 2.5 \times 10^{-4}$ mol/L), H_2O (80 mL), 20 min.; benzyl phenyl ether (1.84 g), H_2O (80 mL), HZSM-5 (0.03 g), 30 min.

(Fig. 2b). We speculate that the higher concentration of HZSM-5 enhances the in situ formed concentrations of phenol and benzyl alcohol and increases so alkylation yields. Note that the TOF of ether hydrolysis in water $(1.1 \times 10^4 \text{ mol mol}_{\text{H}^+\text{H}_2\text{O}}^{-1} \text{ h}^{-1})$ was one magnitude higher than that with HZSM-5 in the aqueous phase $(1.1-1.3 \times 10^3 \text{ mol mol}_{[\text{H}^+]\text{HZSM-5}}^{-1} \text{ h}^{-1}$ (Table 2, Entries 4–6), which is speculated to the fact that liquid protons in the hightemperature water are more accessible than acid sites in the solid zeolite. To verify this hypothesis, BPE conversion with equivalent amount of liquid acid (H₂SO₄) was carried out at the same conditions, attaining an initial comparable cleavage TOF of 1.4×10^3 mol mol_[H⁺]⁻¹ h⁻¹ as HZSM-5 (Table 2, Entry 7 and Supporting information Table S2). Tested at the temperature range from 483 to 543 K, the apparent activation energy of BPE hydrolysis with H_2SO_4 was 163 kJ mol⁻¹, which was 116 kJ mol⁻¹ higher than that with HZSM-5 ($E_a = 47 \text{ kJ mol}^{-1}$) (Fig. 5). The much lower apparent activation energy with HZSM-5 can be ascribed to the added heat of adsorption of BPE on the HZSM-5. The preexponential factor for H_2SO_4 was 6.4×10^{19} molecules $mol_{H^{+1}}^{-1}$, h^{-1} , whereas the corresponding value for HZSM-5 was merely 4.5×10^7 molecules $mol_{[H^+]}^{-1}$ h⁻¹, strongly indicating that the accessible acid sites with liquid H₂SO₄ is much more abundant than the confined solid acid sites in HZSM-5. Having excluded the thermal pyrolysis route on BPE in the aqueous phase, the higher hydrolysis rate in neat water can be also attributed to either OH⁻ ions from ionization of water which can act as base to efficiently catalyze ether hydrolysis [38] or the in situ produced phenol enhances the acidity of high-temperature water during reaction at 523 K.

When 70 wt.% Ni/SiO₂ was introduced to the reaction mixture, Ni catalyzed the specific hydrogenolysis route on BPE to phenol and toluene formation. In addition, the C–O bond cleavage rate (0.1410 mol h⁻¹) was nearly 50 times as fast as the rate in the presence of 4.0 MPa H₂ (0.0028 mol h⁻¹) (Table 2, Entry 8). The bond cleavage TOF of Ni/SiO₂ (1.7×10^4 mol mol_{Surf Ni} h⁻¹) was one magnitude higher than that with 0.03 or 0.15 g HZSM-5 (1.1×10^3 and 1.3×10^3 mol mol_{H⁺|HZSM-5} h⁻¹, respectively). These results imply that Ni atoms are the major active sites for BPE cleavage when Ni and HZSM-5 (Table 2, Entry 9) verifies the hypothesis that the major reaction pathway for C–O bond cleavage of BPE was Ni-catalyzed hydrogenolysis and that the hydrolysis route only contributed to a minor part (Fig. 4).

Combing these results allows us drawing the general reaction pathways on conversion of BPE with different catalyst components

Aqueous phase:



Scheme 1. The major reaction pathways for conversion of BPE with different catalyst components in the aqueous phase in the presence of hydrogen at 523 K.

in the aqueous phase at 523 K. In high-temperature water with or without HZSM-5 addition, hydrolysis is the major pathway for cleaving the C–O bond, and the following C–C coupling of alkylation takes place between the cleaved phenol and alcohol fragments. When Ni is employed with or without HZSM-5, Ni-catalyzed hydrogenolysis dominates throughout the overall C–O bond cleavage reaction (Scheme 1).

3.4. Cleavage of C–O bond of BPE in undecane at 523 K

When changing the aqueous to apolar phase, the fundamental chemistry for cleaving of C-O bond of BPE is changed. Without catalvst either in N_2 or in H_2 atmospheres (4.0 MPa), the C–O bond of BPE was cleaved by pyrolysis in undecane, but not by hydrolysis because of the absence of water. The cleavage rates in undecane were much slower than those in the aqueous phase, i.e., 0.0014 vs. 0.0022 mol h^{-1} in 4.0 MPa N₂, and 0.0019 vs. 0.0028 mol h^{-1} in 4.0 MPa H₂, respectively (Table 3, Entries 1 and 2). This indicates that the rate of ether hydrolysis in water is much faster than pyrolysis of ether in undecane, agreeing with the observation of Klein et al. [19] that in the presence of water, the cleavage rate of BPE was fourfold higher than that during pyrolysis of the neat substrate at 605 K. The conversion reached 9.7% for the thermal pyrolysis of BPE at 523 K for 30 min. in the presence of H₂, and the main products were heavier products (selectivity: 92.6%) as well as small amounts of toluene (selectivity: 3.1%) and phenol (selectivity: 4.3%) (Table 3, Entry 2), indicating that the non-catalytic pyrolysis breaks down the weakest bond of Caliphatic-O of BPE. The heavier products were formed from the free-radical reaction, dominating the thermal pyrolysis process (Scheme 2). When an acid component of HZSM-5 was added in the presence of H₂, the cleavage rate was increased to $0.0050 \text{ mol } h^{-1}$ compared to $0.0019 \text{ mol } h^{-1}$ without catalysts (Table 3, Entry 3). Similarly, such rate with HZSM-5 in undecane $(0.0050 \text{ mol } h^{-1})$ was slower than that in water (0.0090 mol h^{-1}), which infers again that the hydrolysis route in the aqueous phase is much faster than the pyrolysis pathway in undecane.

However, the metallic Ni/SiO₂ selectively catalyzes the hydrogenolysis of C–O bond of BPE with a cleavage rate of 0.2172 mol h⁻¹, which was 114 times as fast as the rate of pyrolysis without catalyst in the presence of 4.0 MPa H₂ (0.0019 mol h⁻¹) (Table 3, Entry 4). Over Ni sites, the primary products were toluene and phenol (selectivity: >80%), while the free-radical products

Table 3	
The effect of gas atmosphere, HZSM-5 (acid), and Ni/SiO_2 (metal) on the reaction of benzyl phenyl ether (H	BPE) in undecane at 523 K.ª

Entry	Active center in gas atmosphere	Conv.	Conv. Selectivity (C%)								Initial rate	TOF (mol mol $^{-1}$ h $^{-1}$)
		(%)	\bigcirc	\bigcirc	OH	o	OH			Heavier products	$(mol h^{-1})$	
1	N ₂	6.8	1.8		3.8					94.4	0.0014	_
2	H ₂	9.7	3.1		4.3					92.6	0.0019	-
3	H ₂ , HZSM-5 $n([H^+]_{HZSM-5}) = 8.0 \times 10^{-6} \text{ mol}$	25.2	3.6		11.0					85.4	0.0050	$6.3\times 10^2 \ mol \ mol_{[H^+]HZSM-5}^{-1} \ h^{-1}$
4 ^{b,c}	H_2 , 70 wt.% Ni/SiO ₂ N ([Surf. Ni]) = 8.5 × 10 ⁻⁶ mol	14.5	45.5	0.6	19.1	5.7	9.9	2.3	3.2	13.7	0.2172	$2.6\times 10^4~mol~mol_{Surf~Ni}^{-1}~h^{-1}$
5 ^b	H ₂ , 10 wt.% Ni/HZSM-5 n ([Surf. Ni]) = 7.4 × 10 ⁻⁷ mol n ([H ⁺] _{HZSM-5}) = 1.0 × 10 ⁻⁵ mol	25.9	32.4	0.6	19.4	2.9	2.7	2.1	3.3	36.6	0.0259	$3.5\times 10^4molmol_{SurfNi}^{-1}h^{-1}$

^a Reaction conditions: Benzyl phenyl ether (1.84 g), undecane (80 mL), HZSM-5 (Si/Al = 45, 0.030 g), Ni/SiO₂ (70 wt.%, 0.010 g), Ni/HZSM-5 (10 wt.%, 0.050 g), gas pressure (4 MPa), 30 min., stirring at 700 rpm.

^b Benzyl phenyl ether (9.20g).

^c 2 min.

Non-polar solvent (undecane):



Scheme 2. The reaction pathways for conversion of BPE with different catalyst components in the non-polar solvent undecane in the presence of hydrogen at 523 K.

were highly suppressed (selectivity: 13.7%) at a conversion of 14.5%. In addition, the partial hydrogenation of aromatic ring of BPE also occurred on Ni/SiO₂ in undecane, producing cyclohexylmethyl phenyl ether (selectivity: 2.3%) and benzyl cyclohexyl ether (selectivity: 3.2%) (Table 3, Entry 4). The bond cleavage TOF of Ni $(2.6 \times 10^4 \text{ mol mol}_{\text{Surf Ni}}^{-1} \text{ h}^{-1})$ was 40 times as fast as that with HZSM-5 (6.3 \times 10^2 mol mol $_{[\rm H^+|\rm HZSM-5}^{-1}$ h^{-1}). It should be addressed that in the non-polar solvent TOF for C-O bond cleavage on Ni/SiO₂ ($2.6 \times 10^4 \text{ mol mol}_{\text{Surf Ni}}^{-1} \text{ h}^{-1}$) was slightly higher than that in the aqueous phase ($1.7 \times 10^4 \text{ mol mol}_{\text{Surf Ni}}^{-1} \text{ h}^{-1}$). It has been consistently demonstrated that Ni surface atoms are the active sites for hydrogenolysis of C-O bond of BPE in the aqueous and apolar solvent (Schemes 1 and 2). The lower activity of Ni in aqueous phase may be attributed to the weaker adsorption of the reacting substrates in the presence of water [39]. It has been reported that in the aqueous phase, the Ni catalyst would deactivate due to water induced formation of Ni-bridged hydroxo species [40]. With Ni/HZSM-5, the major reaction pathway was hydrogenolysis of the C-O bond of BPE in undecane to produce toluene (initial selectivity: 33%) and phenol (initial selectivity: 25%) (Scheme 2). Free-radical reactions via pyrolysis were enhanced after HZSM-5 addition (together with Ni) with selectivity up to 36.6%. With

Ni/HZSM-5 the C–O bond cleavage TOF in undecane $(3.5 \times 10^4 \text{ mol mol}_{\text{Surf Ni}}^{-1} \text{ h}^{-1})$ (Table 3, Entry 5) was much lower in water $(1.1 \times 10^5 \text{ mol mol}_{\text{Surf Ni}}^{-1} \text{ h}^{-1})$, which may be attributed to the fact that BPE is protonated in the high-temperature water which makes the further C–O bond cleavage much easier, which is supported by the DFT calculations discussed in the following part.

3.5. Theoretical calculations for cleavage of C–O bond of BPE in the aqueous and aploar phases

Accompanying with the experimental investigation, DFT calculations explore potential reaction routes for cleaving the C-O bonds of BPE in aqueous and apolar phases. In the aqueous phase, the direct cleavage of the C-O bond of the BPE into benzyl cation $(C_6H_5CH_2^+)$ and phenoxy anion $(C_6H_5O^-)$ was found to be difficult, requiring a high endothermic energy of 238 kJ mol⁻¹. This agrees perfectly with the reported bond strength of C_{aliphatic}-O bond in BPE (234 kJ mol⁻¹) [41]. In an alternative way, BPE was facilitated to be protonated by the adjacent protons, and subsequently, the protonated BPE could be readily cleaved forming phenol and benzyl cation with a low activation barrier of $9.9 \text{ kJ} \text{ mol}^{-1}$ (Fig. 6). Compared with the direct C–O cleavage with a high endothermic energy, the C-O cleavage of the protonated BPE is slightly exothermic. The formed benzyl cation was very active, combining with phenol or water in the aqueous phase in the next step. In essence, in the first route, the benzyl cation combines with phenol to produce 2-benzylphenol or 4-benzylphenol, while in the latter pathway, the benzyl alcohol ($C_6H_5CH_2OH_2^+$) formed via combination of protonated benzyl cation and water is deprotonated to benzyl alcohol. Then, the produced proton is transferred to the neighboring water. Our calculations support the second route. It shows that the coupling between the benzyl cation and water $(\Delta G_{act}^{\circ} = 9.0 \text{ kJ mol}^{-1})$ was almost comparable to that of coupling between the benzyl cation and phenol (ΔG_{act}° = 12.5 and 14.2 kJ mol $^{-1}$, respectively), whereas the deprotonation of $C_6 H_5$ $CH_2OH_2^+$ (ΔG_{act}° = 53.1 kJ mol⁻¹) was much more favored than the other two C–C coupling steps (ΔG_{act}° = 71.6 and 82.4 kJ mol⁻¹, respectively) although the deprotonation step is lightly endothermic. The calculated energy profile of BPE conversion in the aqueous phase (Fig. 6) clearly demonstrates that phenol and benzyl alcohol were the major products while 2-benzylphenol and 4-benzylphenol were formed in minor parts. This is consistent with our experimental observation that hydrolysis dominates for C-O bond cleavage in BPE, while the following C-C coupling reactions played a minor role. Our calculation also shows that the required energy



Fig. 6. Energy profile of benzyl phenyl ether conversion in the aqueous phase calculated by DFT.

was 655.5 kJ mol⁻¹ for forming benzyl and phenoxy radicals from BPE in the aqueous phase, so that the pyrolysis route was not favored in this sense.

In contrast to the major hydrolysis pathway of BPE in water, based on the experimental results, the conversion of BPE followed the pyrolysis route in the apolar solvent such as undecane. Our theoretical calculations support this conclusion as well. It

(a) C-O bond cleavage mode of BPE in undecane



(b) Mechanism of phenol and toluene formation in undecane



Fig. 7. (a) Three C–O bond cleavage modes of BPE in undecane, and (b) proposed mechanism of phenol and toluene formation in undecane.

demonstrated that the dominant intermediates were benzyl and phenoxy radicals in undecane obtained by the C-O bond cleavage of the BPE, due to the much lower bond dissociation energy (184.3 kJ mol⁻¹) compared to that of phenyl and benzoxy radicals $(332.9 \text{ kJ} \text{ mol}^{-1})$ and that of benzyl cation and phenoxy anion (627.7 kJ mol⁻¹) (Fig. 7a). The formed two radicals (benzyl and phenoxy radicals) spontaneously recombined together with an energy drop of ~ 150 kJ mol⁻¹ (Fig. 8), resulted in producing 2-C₆H₅ $OCH_2C_6H_5$ and $4-C_6H_5OCH_2C_6H_5$ radicals. In turn, the H atoms in 2-C₆H₅OCH₂C₆H₅ and 4-C₆H₅OCH₂C₆H₅ radicals stepwise shifted to the O_{radical} atom via H atom transfer forming the final products of 2-benzylphenol and 4-benzylphenol (Fig. 8). The free activation barriers for the H atom transfer were 216.1 and 210.4 kI mol⁻¹ in 2-C₆H₅OCH₂C₆H₅ and 4-C₆H₅OCH₂C₆H₅, respectively. Comparing to the relative low activation barriers $(9.9 \text{ kJ} \text{ mol}^{-1})$ in the hydrolysis path of BPE in water, the activation barriers in the pyrolysis of the BPE in undecane were much higher (184.3 kJ mol⁻¹), which is in line with the experimental results that the rates of BPE conversion were slower in undecane than in water. In addition, the formation of phenol and toluene was thermodynamically favorable in undecane (Fig. 7b). However, the high H_2 dissociation energy results in the quite low concentrations of hydrogen radical without the aid of metals, which eventually leads to a low selectivity to phenol and toluene. In summary, C-O bonds of BPE in undecane are majorly cleaved by pyrolysis for producing phenyl and benzoxy radicals as intermediates, and the subsequent coupling of C-C bonds forms via radical recombination producing 2-C₆H₅OCH₂C₆H₅ and $4-C_6H_5OCH_2C_6H_5$, fitting well with the previous experimental results.

4. Conclusion

In the aqueous phase, the C–O cleavage of BPE proceeds with an ionic pathway at 523 K, but not via a thermal/free-radical route. In the neat water in the absence or the presence of H_2 , the acid (hydronium ions from dissociated water)-catalyzed hydrolysis route dominates, and subsequently, the alkylation between the phenol and alcohol fragments follows to a small extent. In the presence of HZSM-5, both hydrolysis and alkylation rates are substantially enhanced. Ni/SiO₂, in contrast, leads to the quantitative and selective hydrogenolysis of $C_{aliphatic}$ –O bond to form phenol



Fig. 8. DFT calculated energy profile of benzyl phenyl ether conversion in undecane.

and toluene in the presence of H₂. In the presence of metal and acid sites, metal (Ni)-catalyzed hydrogenolysis plays a more important role for cleaving the ether bond in BPE. In apolar undecane at 523 K, non-catalytic pyrolysis cleaves the C_{aliphatic}-O bond of BPE, and thus, the free-radical products dominate. When metals such as Ni/SiO₂ and Ni/HZSM-5 are involved, hydrogenolysis dominates the conversion, markedly suppressing the radical reaction. Ni/SiO₂ leads to higher hydrogenolysis rates in undecane than in water, probably because of the much weaker adsorption of reactants onto active Ni sites in the aqueous phase.

The DFT calculations support the proposed C–O bond cleavage mechanisms in the aqueous and apolar phases. Modeling results show that the protonation of BPE rather than the direct cleavage of the ether bond is the initial primary route in the aqueous phase due to the lower activation energy. In turn the protonated BPE is readily cleaved to form phenol and benzyl cation. Therefore, hydrolysis is substantiated to be the main route for BPE conversion in aqueous phase. In contrast, the radical reaction plays a dominating role in undecane, and the high concentrations radicals generate high concentrations of condensed heavier products. The formed phenol and toluene are present in small concentrations in the pyrolysis process due to the low concentrations of produced hydrogen radicals without metals.

Acknowledgments

J.H. gratefully acknowledges for the support from the graduate school (Faculty Graduate Center of Chemistry) of the Technische Universität München and the Elite Network of Bavaria (Graduate School NanoCat). D.M. and J.A.L. thank for the support from the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. Pacific Northwest National Laboratory (PNNL) is a multiprogram national laboratory operated for DOE by Battelle. Computing time was granted by the grand challenge of computational catalysis of the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) and by the National Energy Research Scientific Computing Center (NERSC). EMSL is a national scientific user facility located at Pacific Northwest National Laboratory (PNNL) and sponsored by DOE's Office of Biological and Environmental Research.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.10.024.

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