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Hydrogenolysis/hydrogenation of diphenyl ether as a model decomposition reaction of lignin from biomass in pressurized CO_2/water condition

Maya Chatterjee[a,*], Takayuki Ishizaka[a], Hajime Kawanami[a,b,*]

[a] Microflow Chemistry Group, Research Institute for Chemical Process Technology AIST Tohoku, 4-2-1, Nigatake, Miyagino-ku, Sendai, 983-8551, Japan
[b] CREST, Japan Science and Technology (JST), 4-1-8, Honcho, Kawaguchi, Saitama, 332-0012, Japan

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ABSTRACT

Catalytic hydrogenolysis of the C—O bond of diphenyl ether (a lignin model compound) was investigated as a function of hydrogen pressure in $scCO_2$ medium in the presence of water. Using commercially available Rh/C catalyst, the C—O bond cleavage of diphenyl ether mainly results phenolic monomer at 80 °C. Hydrogen pressure is one of the key parameters because (i) C—O bond cleavage and the hydrogenation of aromatic rings are two competitive reactions; very sensitive to hydrogen pressure and (ii) hydrogen has complete solubility in $scCO_2$. Therefore, a critical control of hydrogen pressure was essential to reach the targeted cleavage of the C—O bond when the reaction was conducted in $scCO_2$ medium under pressurized condition. Depending on the hydrogen pressure, a significant change in the ratio of monocyclic:bicyclic products from 91:9 (0.2 MPa) to 58:42 (2 MPa) was revealed in the shortest reaction time of 5 min. Thus, low hydrogen pressure was the effective choice for the scission of the C—O bond, whereas higher hydrogen pressure hydrogenate the aromatic ring due to the higher coverage of hydrogen on the catalytic surface. Amount of the catalyst (catalyst:substrate ratio) displayed a subtle effect on the breakage of the C—O bond. A threshold ratio of 1:5 was preferred under the present reaction condition as the increased amount hampered the substrate:water ratio and hydrogenation of the aromatic ring occurred. In addition, as the change in temperature is associated with the change in the physical properties of $scCO_2$, hence, the effect on the transformation of DPE was complicated and difficult to explain. Furthermore, different organic solvents as neat, along with CO_2 and with water also has substantial impact on the rapture of C—O bond. The obtained results from the solvent studies again proved that $scCO_2$ along with water was the best choice for C—O bond breakage and water is the driving force to mediate the reaction. In addition, a combination catalyst (Ni+Rh) was also tested for the same reaction under the similar working condition. Preliminary results suggested a synergistic effect in terms of the selectivity of monocyclic compounds.

1. Introduction

Lignocellulosic biomass is the most abundantly available plant materials on earth and has various sources such as hardwood, softwood and herbaceous plants. It is cheaper than starch and sucrose based materials. Lignocellulosic biomass is a composite material, contains 15–30% of lignin by weight and ~40% by energy [1–4]. Lignin is a three dimensional network polymer comprised variously linked phenylpropane units. The phenylpropane units are connected by C—C and ether linkages such as β-O-4, β-1, β-5, α-O-4, 4-O-5 etc. with strength and stability [5]. Among them 4-O-5 is the strongest one with bond dissociation energy of 75.1 Kcal/mol. Depolymerisations of lignin is an important strategy because it generates valuable chemicals or low molecular mass feedstocks [6] and challenging because of the stability of the ethereal bond [7–14]; generally conducted as acid and base catalysed reactions [15]. Ethereal compound is one of the main components of lignin, different strategies were developed to break the C—O bond, albeit different catalysts (noble metals or non-noble metals) or methods which can selectively target the functionality of the aryl ether bond for removing oxygenated group from aryl ring [16–20] in the presence of hydrogen. However, during the cleavage of C—O bond main competitor is the hydrogenation of the aromatic ring as the dissociation energy of C—O bond is very high of 218–314 kJ mol^{-1} [21] and it is difficult to break down the ether bond without hydrogenating

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* Corresponding authors.
E-mail addresses: c-maya@aist.go.jp (M. Chatterjee), t-ishizaka@aist.go.jp (T. Ishizaka), h-kawanami@aist.go.jp (H. Kawanami).

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the aromatic ring. Therefore, to achieve desired cleavage of C—O bond, application of harsh reaction condition was the only choice, which resulted a mixture of several compounds. Different noble and non-noble metal catalysts were attempted for the breakage of C—O bond. Among the non-noble metal supported catalysts [22,23], Ni was used mostly in the hydrogenation reactions due to its low cost and moderate performance. In 2011, a remarkable work of Sergeev and Hartwig suggested a Ni based homogeneous catalyst $Ni(COD)_2$ for successful cleavage of aryl C—O bond in the presence of a specific carbene ligand and NaOBu as base [24]. In addition, the same group also investigated the selective hydrogenolysis of aryl ethers using homogeneous catalyst formed in-situ from the well-defined soluble nickel precursor $Ni(COD)_2$ or Ni-$(CH_2TMS)_2(TMEDA)$ and a base additive (tBuONa) in *m*-xylene at 120 °C within the reaction time of 96 h without any additional dative ligand [25]. Following their footsteps, heterogeneous catalysts, which are considered as not very selective and require higher temperature for the cleavage of the C—O bond was the subject of study. Zhao and Lercher successfully introduced Ni/SiO_2 catalyst containing 60% Ni for efficient cleavage of aryl ethers in the presence of hydrogen in aqueous medium [26]. Ni/ZSM-5 was adopted for the hydrogenolysis of real lignin as well as model compounds under a comparatively mild condition (250 °C, 5 MPa) [27]. Moreover, iron (III) acetylacetonate [28], integrated Ni nanoparticles supported on porous SiC composites [29] were also reported for the desired cleavage of the C—O bond of aryl ether to improve the catalytic activity or reusability of the catalyst. Hydrolysis of lignin model compound was another approach to cleave the C—O bond conducted in supercritical water using heterogeneous catalysts $Ni/ZrO_2/K_2CO_3$, which still required high temperature of 240–400 °C and 25–32 MPa of hydrogen [30]. Thus, from the existing literature, it was evident that Ni-based catalysts (mainly homogeneous) are potential candidate with high efficiency for the rapturing of C—O bond under a comparatively mild reaction condition. However, homogeneous Ni catalyst suffers difficulties of product separation, requirement of expensive ligands, and reusability problems. On the other hand, some of the Ni based heterogeneous catalysts are difficult to handle because of their air sensitivity and in other cases large amount of metal was necessary to achieve best performance [31].

The offerings of heterogeneous catalysts tempted us to develop a simple and convenient method for hydrogenolysis of aryl C—O bond of diphenyl ether. Noble metal catalysts are widely studied for their excellent activity in various reactions also used in the conversion of lignin into different phenolic compounds [32,33]. Thus, hydrogenolysis of diphenyl ether (DPE), which mimic the 4-O-5 linkages was conducted over the commercially available Rh/C as heterogeneous catalyst in supercritical carbon dioxide ($scCO_2$)/water system [34,35]. The use of diaryl ether model compound represents a firm test of the effectiveness of the catalyst on the cleavage of ether linkages. The use of $scCO_2$ as reaction medium has several unique advantages such as clean product separation, high product selectivity, non-toxicity, non-flammability etc. and most importantly, in the presence of water, CO_2 creates an acidic environment [36,37] would be the responsible factor behind the cleavage of the C—O bond [38]. Instead of expensive metal hydride, molecular H_2 was used as the source of hydrogen. In the studied process, under a mild reaction condition activated hydrogen breaks aryl C—O bond at 80 °C within the reaction time of 5 h.

In our previous report [35], we observed that the transformation of DPE involves C—O bond hydrogenolysis/hydrolysis and the hydrogenation of aromatic ring, where water played a significant role. When using only water or CO_2, hydrogenolysis of C—O was hampered, hence a combined effect was required. Similarly, hydrogen is another important parameter to achieve successful cleavage of the C—O bond because hydrogen has complete solubility in $scCO_2$ and increased concentration in the reaction medium is inevitable, which require a careful control. In this work we attempted to clarify the role of hydrogen in terms of product distribution and studied the effect of temperature, the amount of substrate as well as different organic solvents instead of water along with CO_2 on the C—O bond cleavage. In addition, the same reaction was also explored in the presence of a Ni-Rh combination catalyst.

2. Experimental

2.1. Materials

All chemicals were obtained commercially. Diphenyl ether and phenol were from Wako Pure Chemicals. 5 wt.% Rh/C and cyclohexyl phenyl ether were obtained from Sigma-Aldrich. Carbon dioxide (>99.99%) from Nippon Sanso Co. Ltd. was used for the reaction.

2.2. Catalytic activity

The conversion of the model compound was conducted in a 50 ml stainless steel batch reactor containing required amount of the catalyst, substrate (wt. ratio of catalyst:substrate = 1:5) and water. The reactor was placed in an oven with fan heater to maintain the constant temperature. After reaching the desired temperature, hydrogen of required pressure was first introduced into the reactor. Liquid CO_2 was charged into the reactor using a high pressure liquid pump (JASCO). The reaction mixture was stirred continuously with a Teflon coated magnetic bar during the reaction. After the reaction, the reactor was cooled with ice-water and depressurized carefully by the back-pressure regulator. The product mixture was separated from the catalyst simply by filtration. GC/MS (Varian Saturn 2200) was used for identification and quantitative analysis of the product mixture. Quantification of the products was obtained by a multi-point calibration curve for each product. The selectivity to each product was calculated by the following expression $S_i = C_i/\sum Cp$, where C_i is the concentration of the product ‘i’ and $\sum Cp$ is the total concentration of the product.

3. Results and discussion

Scheme 1 represent possible reaction pathways of the conversion of DPE under the studied reaction condition ($P_{CO2} = 10$ MPa, $P_{H2} = 0.5$ MPa, temperature = 80 °C, time = 5 h and water = 4 ml). There are three different routes of conversion: (i) hydrogenolysis, which results an equimolecular mixture of monocyclic compounds such as phenol (PhOH) and benzene (Bz) followed by the hydrogenation to cyclohexanone (CHO)/cyclohexanol (CHOH) and cyclohexane (CH), respectively. (ii) Hydrolysis generates two molecules of PhOH and subsequently hydrogenated to CHOH and (iii) hydrogenation of aromatic rings; DPE can be converted to a partial aromatic ring hydrogenated product cyclohexyl phenyl ether (CHPE), followed by the formation of a completely hydrogenated dicyclohexyl ether (DCHE). Presence of hydrogen was necessary for the conversion of DPE, because there was no reaction in the absence of hydrogen.

3.1. Dependence of the reaction path on hydrogen pressure

To investigate the effect of hydrogen pressure, the reaction was conducted at different hydrogen pressure (0.2–2 MPa) keeping other parameters constant (Fig. 1). Except the very low pressure of 0.2 MPa, DPE was completely converted to the corresponding reaction products within the reaction time of 5 h. The effect of hydrogen pressure on product distribution was significantly prominent. For instance, the selectivity of CHOH was increased from 78.4% to 96%

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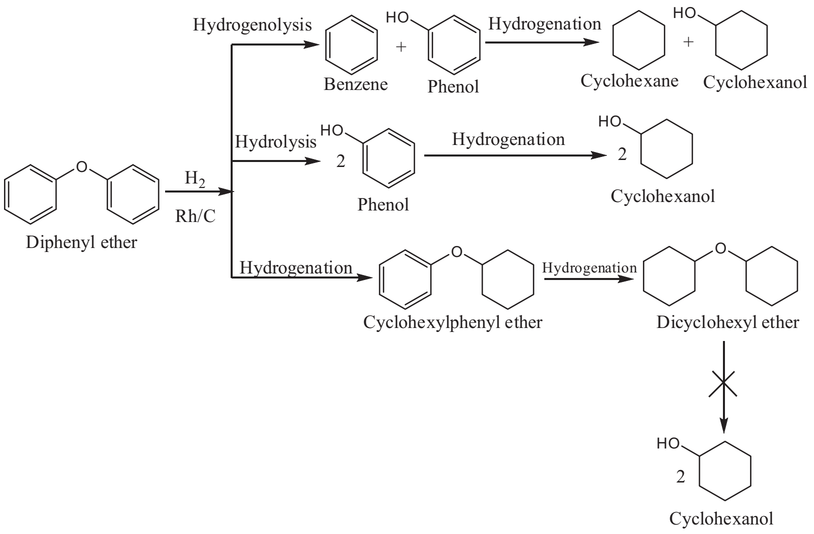

Scheme 1. Possible reaction path of DPE conversion in $scCO_2$/water.

as the pressure changes from 0.2 to 0.5 MPa and then decreased to 31% when the pressure reached to 2 MPa. On the other hand, the selectivity of DCHE was <5% at 0.2 MPa and increased to 68.5% at the higher pressure of 2 MPa. According to the Scheme 1 DPE could follow three routes such as hydrogenolysis, hydrolysis and hydrogenation to transform into different products. Monocyclic products such as CHOH, CHO and CH/Bz were produced through the hydrogenolysis of C—O bond or via hydrolysis, whereas, bicyclic products (CHPE and DCHE) could be generated via hydrogenation. Therefore, low hydrogen pressure was required for the breaking of C—O bond to generate monocyclic products. Contrarily, bicyclic product such as DCHE was observed at higher pressure (>0.5 MPa) in $scCO_2$/water medium. No partially hydrogenated product (CHPE) was detected in the final products. The solubility of hydrogen in the reaction medium is main concern when the reaction was conducted in $scCO_2$ because hydrogen compete with the substrate. Hence, an effective control of hydrogen pressure is necessary to generate monocyclic compounds. Otherwise, increased hydrogen pressure will enhanced the amount of hydrogen in the reaction medium. As a result, hydrogenation of the aromatic ring could be easier instead of the cleavage of C—O bond. Therefore, it is clear that hydrogen pressure has significant influence on the reaction path of DPE conversion.

From the scenario presented above it is difficult to get an insight about the actual reaction trend occurring in different hydrogen pressure. A time dependent course of the reaction was studied at different hydrogen pressure and the results are shown in Fig. 2a–d.

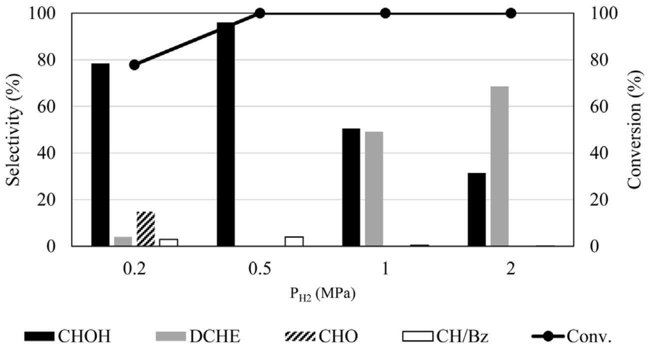

Fig. 1. Effect of hydrogen pressure on the cleavage of C—O bond and hydrogenation of aromatic rings. Reaction condition: P_{CO2} = 10 MPa; catalyst: substrate = 1:5; temp. = 80 °C, reaction time = 5 h and water = 4 ml.

Fig. 2a evidences the transformation of DPE at the lower pressure of 0.2 MPa within the reaction time of 5 min to 5 h leaving other conditions similar (temperature = 80 °C, P_{CO2} = 10 MPa and water = 4 ml). Results revealed that 25.2% of DPE was converted within the reaction time of 5 min and the maximum conversion of 77.8% was reached in 5 h. Considering the product distribution, in the beginning, the product mixture was consisted of monocyclic compounds such as CHOH (41.9%), CHO (40.2%) and CH (3.5%). No phenol was detected even in the shortest reaction time (5 min) because of the faster conversion to CHOH and CHO via two parallel reactions. As the time progressed the conversion of DPE was increased to 77.8% followed by the enhancement of the selectivity of CHOH from 41.9% to 78.4%. However, the selectivity of CHO was dropped from 40.2% to 14.7% with the increased selectivity of CHOH. This result suggested that the hydrogenation of CHO to CHOH was favorable under the present reaction condition. Final product mixture after 5 h of reaction contains 78.4% of CHOH, 14.7% of CHO, 2.9% of CH/Bz. Noteworthy, the selectivity of deoxygenated monocyclic compound remain unaltered. On the other hand, bicyclic products (4.2% DCHE and 10.2% CHPE) were also detected in the product mixture after 5 min. Interestingly, CHPE was completely diminished within 30 min, and the selectivity of DCHE slightly increased to 10%. There was almost no change in the selectivity of DCHE even after 5 h of reaction. To interpret this result, it could be suggested that at very low pressure of hydrogen cleavage of the ethereal C—O bond was the preferred route because substrate has better coverage on the catalyst surface rather than hydrogen.

At 0.5 MPa, the conversion of DPE was 32% within the reaction time of 5 min, and complete transformation required 30 min. (Fig. 2b). Main components of the product mixture consisted of CHOH with the selectivity of 52.9% along with 31.6% of CHO and 3.2% of CH after 5 min of reaction. Noticeably, the selectivity of CHOH was improved compared to 0.2 MPa. Within the reaction time of 30 min, CHO was completely converted to CHOH because of the increased hydrogen pressure and consequently there was an increased selectivity of CHOH, which reached to 96%. In addition, partially hydrogenated CHPE and DCHE were also detected in the product mixture with very low selectivity of 5.1 and 6.4%, respectively after 5 min but undetected in the final mixture. A careful observation revealed that even at 0.5 MPa, cleavage of the C—O bond was the main route of conversion as confirmed by the calculation of the molar ratio of monocyclic:bicyclic compounds in the beginning (90:10) and after completion of the reaction (100:0).

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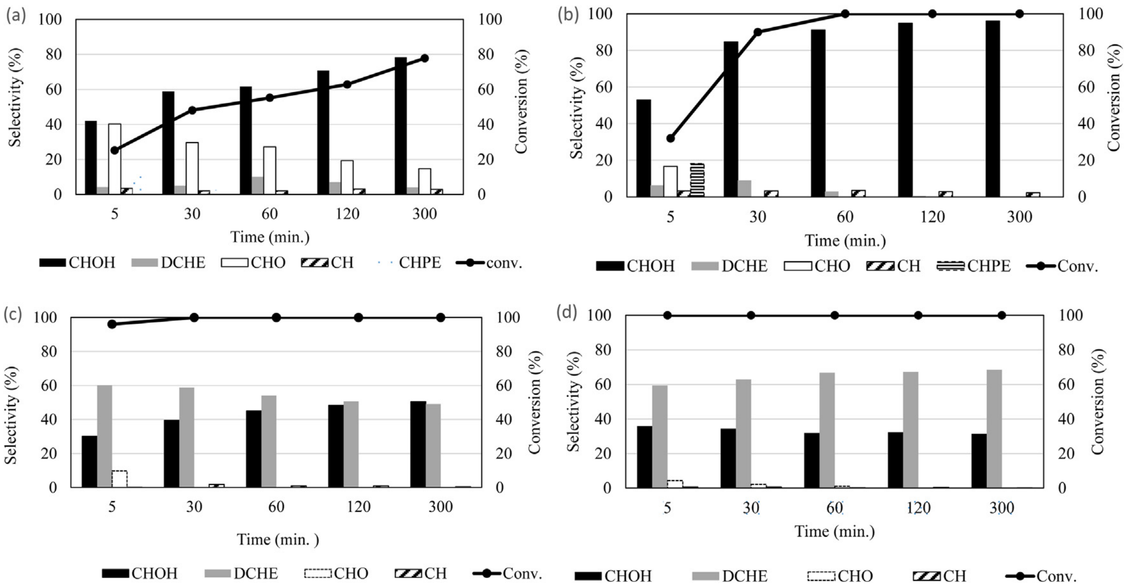

Fig. 2. Time course of the reaction depending on hydrogen pressure: (a) 0.2 MPa, (b) 0.5 MPa, (c) 1 MPa and (d) 2 MPa. Reaction condition: P_{CO2} = 10 MPa; catalyst: substrate = 1:5; temp. = 80 °C and water = 4 ml.

Fig. 2c revealed the change in the catalytic performance of Rh/C catalysts after applying 1 MPa of hydrogen pressure in the reaction time of 5 min to 5 h. The reaction was very fast and 96% of DPE was converted within 5 min. As the concentration of hydrogen increased the hydrogenation reaction was the main route of the conversion, reflected from the composition of the product mixture, which contains mainly DCHE with the selectivity of 60.2%. In addition, 30% of CHOH and 9.8% of CHO were also observed as C—O bond cleaved product. It is intriguing that after 5 h of reaction, the selectivity of CHOH was improved to 50% while the selectivity of DCHE was decreased to 49%, thus, a possibility of the conversion of DCHE to CHOH might be speculated during the course of the reaction. However, when we conducted a separate reaction with CHPE, except DCHE no other products were detected even after extending the reaction time of 18 h as fully saturated ethers are difficult to breakdown and the possibility of the conversion of DCHE to CHOH remain unexplained in the studied working condition.

The time course of the DPE conversion at 2 MPa again presents the same scenario of 1 MPa (Fig. 2d). Within 5 min. DPE was completely converted mainly into DCHE (59.4%). The selectivity of monocyclic and bicyclic products were unaltered after 5 h of reaction. Interestingly, exclusive formation of DCHE was not observed even after application of higher hydrogen pressure indicating not enough hydrogen around the aromatic ring for its conversion and expect a competition between the C—O bond cleavage and the hydrogenation of the aromatic ring [27].

Depending on the hydrogen pressure, we investigated the turnover frequency (TOF) of C—O bond cleavage (TOF $_{C–O}$) and hydrogenation of aromatic ring (TOF$_H$) within the shortest reaction time of 5 min and after 5 h of reaction (Fig. 3). Results reveal that TOFs depend heavily on the hydrogen pressure. In the beginning of the reaction, an extremely high TOFs should be noted. For instance, when the hydrogen pressure was increased from 0.2 to 2 MPa, the TOF $_{C–O}$ was changed from 365 h^{-1} to 641 h^{-1}, which reaches a maximum of 1054 h^{-1} at 0.5 MPa. On the other hand, the TOF$_H$ was significantly enhanced from 68 to 527 h^{-1} along with the hydrogen pressure of 0.2–2 MPa. Noticeably, for the breakage of C—O bond, TOF reaches a maximum and then decreased indicating the preference for low hydrogen pressure, whereas, TOF$_H$ was increased constantly reflects the higher pressure favored hydrogenation of the aromatic rings. However, in any case, rate of C—O bond cleavage (TOF $_{C–O}$) was higher than the TOF$_H$ suggesting the hydrogenolysis and hydrolysis were two major routes in the transformation of DPE in the present system. Furthermore, TOFs after 5 h of reaction reduces significantly for each cases (TOF $_{C–O}$ and TOF$_H$). The maxima of TOF $_{C–O}$ and TOF$_H$ were dropped to 102 h^{-1} (0.5 MPa) and 15 h^{-1} (2 MPa), respectively, which might be attributed to the scarcity of the substrate in the system. Moreover, the catalyst in the system was still active and can be restarted again by the addition of the reactant.

3.2. Effect of the amount of substrate

Accumulating the above-mentioned experimental results it could be inferred that after complete consumption of DPE selectivity of monocyclic and bicyclic products remain almost same even after extending the reaction time and the rate of the reaction (TOF) was decreased considerably. Thus, we consider to study the impact of the amount of substrate on the catalytic performances and the results are shown in Fig. 4. Maintaining the other operating conditions constant, catalyst/substrate ratio was varied from 1:3 to 1:50. Result shows complete conversion of DPE was achieved up to the catalyst:substrate ratio of 1:30 within the reaction time of 5 h, but conversion dropped to 48% when the ratio of 1:50 was used. Moreover, the catalyst:substrate ratio also influenced the selectiv-

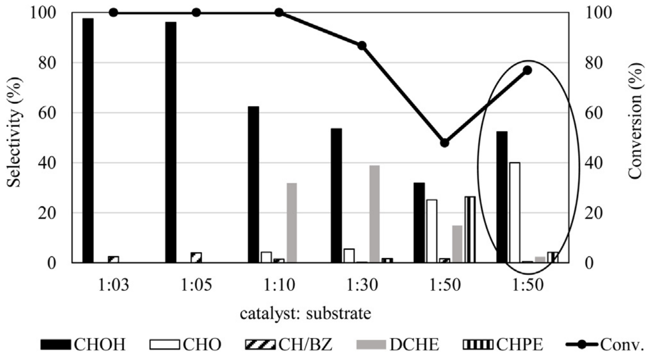

Fig. 3. Variation of the amount of substrate. Reaction condition: P_{CO2} = 10 MPa, P_{H2} = 0.5 MPa, time = 5 h, temp. = 80 °C and water = 4 ml.

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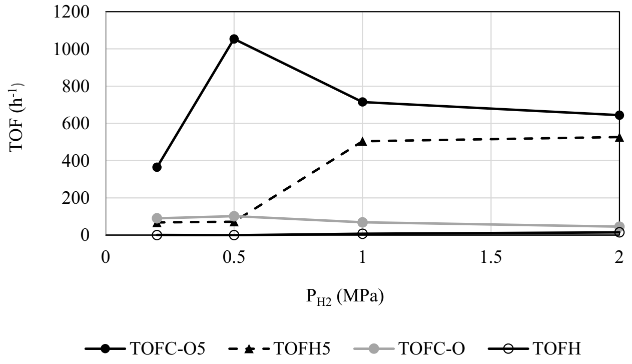

Fig. 4. Comparison of TOF $_{C—O}$ and TOF$_H$ at 5 min and 5 h of reaction. TOF $_{C—O5}$ and TOF$_{H5}$ represents 5 min of reaction time; TOF $_{C—O}$ and TOF$_H$ = reaction time 5 h; Reaction condition: P_{CO2} = 10 MPa, P_{H2} = 0.5 MPa, catalyst: substrate = 1:5, temp. = 80 °C and water = 4 ml.

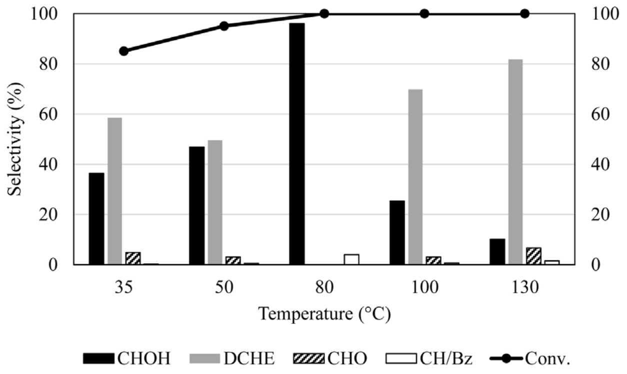

Fig. 5. Effect of temperature on C—O bond cleavage. Reaction condition: P_{CO2} = 10 MPa, P_{H2} = 0.5 MPa, time = 5 h, catalyst:substrate = 1:5 and water = 4 ml.

ity of monocyclic and bicyclic compounds. Very high selectivity of CHOH (96%) was detected until catalyst:substrate ratio of 1:5 and then dropped sharply to 30.9% for 1:50, whereas the selectivity of CHO increased from 0 to 25.2% under the selected condition. This result implied the very fast conversion of PhOH formed by the breakage of the C—O bond even in the highest catalyst:substrate ratio, which can be converted to CHOH and CHO simultaneously. However, increased selectivity of CHO reflected that there was not enough surface hydrogen to convert CHO to CHOH [39]. On the other hand, Generation of bicyclic products such as CHPE and DCHE were boosted along with the increased amount of substrate in the system; hydrogenated products CHPE and DCHE appeared with highest selectivity of 26.4% (1:50) and 38.9% (1:30), respectively. From the experimental reactivity trend it is clear that with increasing the amount of substrate, the reaction time for complete consumption of DPE varied and restricted the formation of C—O bond cleavage product. It is noteworthy that the conversion was low of 48% and the product mixture still contains CHO and CHPE even after 5 h, which suggested the deficiency of hydrogen in the medium due to the higher coverage of the substrate on the catalyst surface.

From the above results it seems monocyclic products still maintained higher selectivity in comparison with the bicyclic one even with the very high catalyst:substrate ratio. However, if we compare the TOFs between the cleavage of C—O bond (TOF $_{C—O}$) and the hydrogenation (TOF$_H$), using the catalyst:substrate ratio of 1:50, the TOFs are turned out as comparable: TOF $_{C—O}$ = 7.2 h^{-1} and TOF$_H$ = 5.8 h^{-1}. Hence, an increased amount of substrate restricted that C—O bond cleavage and enhance the possibility of hydrogenation of aromatic ring. When the catalyst:substrate ratio was increased it hampered the CO_2:substrate (1:0.005 to 1:0.04), H_2:substrate (1:10 to 1:1) as well as H_2O:substrate (1:0.004 to 1:0.036) ratio. After a series of experiments it could be inferred that changing the CO_2 and the H_2 pressure has negligible effect on the increased amount of substrate. From our previous work [35], it has been found that presence of water is essential for the scission of the C—O bond and a threshold amount of water was necessary to achieve monocyclic products with very high selectivity. Hence, an extended experiment was conducted using catalyst:substrate ratio of 1:50 by increasing the amount of water from 4 to 8 ml at 80 °C and the reaction time of 5 h. Interestingly, the conversion was increased from 48% to 77% with the addition of water. Additional water also changes the product distribution, which consists of 92.9% (CHOH = 52.3%, CHO = 40%, CH/Bz = 0.6%) and 7. 1% (DCHE = 2.4%, CHPE = 4.7%) of monocyclic and bicyclic compounds, respectively (Fig. 4; marked part). These findings again proved that water is the main reason behind the cleavage of the C—O bond of DPE. The role of water is critical here because DPE is completely insoluble in water. To understand the role of water an on-water reaction can be proposed in which the reaction occurred on the water organic interface and the relative interfacial hydrogen bonding is the key factor for the reaction as the reactant is insoluble in water [40–42].

3.3. Reaction temperature vs. C—O bond cleavage

To investigate the effect of temperature, the reaction was conducted at various temperature of 35, 50, 80, 100 and 130 °C and the results are shown in Fig. 5. Unlike the reactions in liquid solvent, there was no straight forward effect on the catalytic activity when the reaction was conducted in $scCO_2$. Noticeably, there was no effect of temperature on the conversion. Independent to the temperature, DPE was completely converted to the corresponding products. However, the change in temperature manifested an interesting result in terms of product distribution. At lower temperature, hydrogenation and C—O bond breakage co-existed. As the temperature increased the selectivity of monocyclic product (CHOH, CHO and CH/Bz) increased and reached a maximum of 100% at 80 °C; dominating the C—O bond cleavage. No hydrogenated product was detected in this condition. To explain this result it could be suggested that hydrogenation of aromatic ring was the most favorable process at the lower temperature due to the presence of large amount of hydrogen, but C—O bond has higher energy, thus, higher temperature has beneficial effect on the cleavage of C—O bond. Furthermore, it is reported that lower temperature and high hydrogen pressure prefers hydrogenation instead of hydrogenolysis [43,44]. Therefore, one could expect a better performance regarding the generation of monocyclic compounds after further elevation of temperature. Unfortunately, the increased temperature of >80 °C causes hydrogenation of the aromatic ring rather than C—O bond rapturing, consequently the selectivity of monocyclic product was dropped substantially from maximum of 96–10% with the change in temperature from 80 to 130 °C. As the reaction was conducted in $scCO_2$ medium under the fixed pressure condition when the temperature increases there is every possibility that it could disturb the solubility of CO_2 in water and then the system behaves like no water system which favored hydrogenation.

3.4. Effect of solvent

As a part of the catalytic system, reaction medium also needs attention to the cleavage of the C—O bond. Wang and Rinaldi [45] first described the effect of different organic solvents on the hydrogenolysis of DPE using Raney Ni catalyst and suggested that solvent is an important part of the reaction, which strongly influenced the catalytic activity. To study the effect of the reaction

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Table 1
Impact of different organic solvents on C—O bond cleavage.

Entry	Solvent	Conv. (%)	Selectivity (%)				
			CHOH	DCHE	CHPE	CHO	CH/Bz
Solvent (neat)							
1	EtOH	14.0	1.5	17.9	66.1	0.8	–
2	MeOH	100.0	22.5	43.4	–	6.7	–
3	Propanol	100.0	30.2	23.9	–	–	0/11.6
4	THF	100	26.6	65.1	–	–	8.3/0
5	Hexane	100.0	8.7	91.3	–	–	–
Solvent + CO_2							
6	EtOH	3	–	–	100	–	–
7	MeOH	5	–	11.0	89.0	–	–
8	Propanol	94	19.3	57.3	2.1	10.8	9.7/0
9	THF	100.0	23.4	–	61.2	10.9	5/0.3
10	Hexane	18.0	3.9	26.9	61.5	3.9	1.8/1.7
Solvent + H_2O							
11	EtOH	100.0	54.2	2.4	–	13.0	0.3
12	MeOH	57.0	38.9	18.2	11.5	29.0	1.6/0.8
13	Propanol	100.0	100.0	–	–	–	–
14	THF	95.5	44.9	34.9	–	9.9	4.5/0
15	Hexane	100.0	27.7	70.6	–	1.1	2.3/0

Reaction condition: P_{CO2} = 10 MPa, P_{H2} = 0.5 MPa, time = 5 h, temp. = 80 °C, catalyst:substrate = 1:5 and water = 4 ml.

medium on the conversion of DPE under the present reaction condition, the reaction was conducted in the neat organic solvents (methanol, ethanol, propanol, tetrahydrofuran and hexane), organic solvents + CO_2 and organic solvents + H_2O at 80 °C and hydrogen pressure of 0.5 MPa (Table 1). From the results it is evident that except ethanol (14%) complete conversion of DPE was achieved for all other solvents in neat condition (Table 1: Entry 1–5). These results indicate that solvent has strong impact indeed. Considering the selectivity of targeted monocyclic products (CHOH, CHO and CH) varies from 2.3 to 41.6%, however, the selectivity range of bicyclic products (DCHE and CHPE) were 23.1–91.3%. The selectivity orders for monocyclic and bicyclic compounds are: propanol > THF > methanol > hexane > ethanol and hexane > THF > methanol > propanol > ethanol, respectively. Thus, it could be predicted that hydrogenation of the aromatic ring was the major route of DPE transformation because of the possible change in the mode of adsorption of the substrate. In the presence of CO_2, the conversion was very poor in methanol (5%), ethanol (3%) as well as in hexane (18%), but propanol and THF provide very high conversion of 94% and 100%, respectively (Table 1: Entry 6–10). The solubility of CO_2 in ethanol and methanol were comparatively lower than in propanol and THF and accordingly CO_2 in presence of THF offers best environment in terms of mass transfer limitation, consequently higher activity [46,47]. The organic solvents in association with CO_2, shows very high selectivity of bicyclic products especially CHPE (61.5%). Analyzing the obtained data on product distribution evidences that hydrogenation of aromatic ring was the main route of DPE conversion in the solvent + CO_2 and the selectivity order was same for both of mono and bicyclic compounds (THF > Propanol > hexane > methanol ≈ ethanol). It should be addressed that in the presence of organic solvents CO_2 can form CO_2-expanded liquid, which improved the transport properties and increased the solubility of reactant gasses such as hydrogen, which facilitate the hydrogenation reaction [48–51]. Clearly THF offers better performance in terms of activity and selectivity (Table 1; Entry 9). The scenario changed when those solvents were used along with H_2O. Higher conversion was detected in each solvent and follows the order of ethanol ≈ propanol ≈ hexane > THF > methanol (Table 1: Entry 11–15). Regarding the product distribution, propanol shows highest selectivity of 100% for CHOH and except hexane in each case monocyclic products were the major part of the mixture and the selectivity order was: propanol > methanol ≈ ethanol > THF > hexane. Among the selected organic solvents, alcohols are miscible in water, THF has comparatively low solubility and hexane shows lowest solubility. From the selectivity order it is clear that miscibility of the organic solvent is an important part of the reaction. The developed method for the conversion of DPE to monocyclic compound using Rh/C catalyst revealed that the presence of water changes the mode of reaction from hydrogenation to hydrogenolysis. Thus, water is not only a spectator for this system, it could dictate the product selectivity. Mechanism behind the cleavage of the C—O bond of DPE in $scCO_2$/water medium is critical. Previously, we observed that water in the presence of CO_2 influenced the pH of the medium and consequently the C—O bond cleavage. However, water in combination with organic solvent (miscible) also results monocyclic compounds. Thus, it could be predicted that solvents like water cannot absorb directly on the Rh surface, but it can modify the surface by creating a hydrophilic environment and thereby a favorable situation for the adsorption of DPE via C—O bond followed by the enhanced selectivity of monocyclic compounds [52,53].

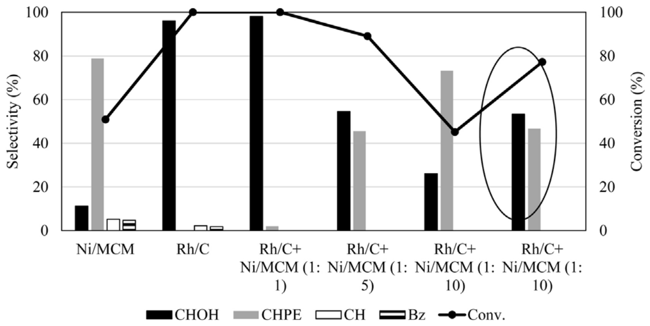

Fig. 6. Ni-Rh combination catalysts for DPE conversion in $scCO_2$/water medium. Reaction condition: P_{CO2} = 10 MPa, P_{H2} = 0.5 MPa, temp. = 80 °C, time = 5 h, catalyst:substrate = 1:5 and water = 4 ml.

3.5. Reactivity of combination catalyst

We already proved that the use of Rh/C as a supported noble metal catalyst is an effective choice for the cleavage of the C—O bond under a mild reaction condition and there was no reaction without any catalyst. Among the non-noble metal catalysts, Ni is

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the most preferred and efficient for hydrogenolysis of C—O bond in the form of homogeneous or heterogeneous way [54–59]. However, under the present working condition, Ni catalyst performed well on the conversion of DPE, but not in the hydrogenolysis of the C—O bond. Bimetallic catalysts are sometimes reported as better performer in terms of hydrogenolysis of C—O bond. There are several reports on bimetallic catalysts on different supports [54–60]. Zhang et al. reported that instead of pure Ni, a combination of Ni with other metals such as Au [61] and Ru, Rh and Pd gave better results [62]. It is well-known that a combination of two different metals significantly change the catalytic activity in comparison with their individual counterpart [63]. Here, our intention is to try a simple approach to investigate the effect of two different catalysts after mixing them together. If mechanical mixing results synergism it could be a guide to the probable effectiveness of bimetallic catalyst. Hence, a series of catalysts were prepared by the mechanical mixing (wt./wt.) of Rh/C and Ni/MCM-41 of different ratio to perform the reaction under the selected condition (temperature = 80 °C, $P_{CO2} = 10$ MPa, $P_{H2} = 0.5$ MPa, water = 4 ml, time = 5 h) and the results are shown in Fig. 6. To avoid the complexity arises from Ni salt and support material, Ni supported on inert material like MCM-41 was used. Fig. 6 shows a comparison of only Rh and Ni catalysts with the different combination of Ni and Rh catalysts for the conversion of DPE. Individually, 50.9% DPE was converted to bicyclic (CHPE) and monocyclic (CHOH) products with the selectivity of 78.9% and 11.2%, respectively, using Ni/MCM-41. On the contrary, DPE was completely converted to 96% of CHOH and 4% of CH/Bz via hydrogenolysis/hydrogenation over Rh/C. The experimental data obtained under identical reaction condition shows a significant difference in the behavior of the catalytic activity when Rh/C and Ni catalyst were mixed together. We conducted the reaction using Rh/C and Ni/MCM-41 mixed in different ratios of 1:1 to 1:10 under the same reaction condition. Starting the reaction with 1:1 (Rh/C:Ni/MCM-41) mixture; complete conversion and a very high selectivity to CHOH (98%) was evidenced along with the formation of CHPE (2%) indicating the predominate effect of Rh. Now, if the ratio was changed from 1:1 to 1:5, the conversion dropped to 89% and then further reduced to 45.2% as the ratio was changed to 1:10 shows that the absence of a synergistic effect on the conversion of DPE after combining the two catalysts. Considering the product distribution, the product mixture contains only CHOH (monocyclic) and CHPE (bicyclic). No deoxygenated monocyclic products and completely hydrogenated products were detected. Mixing gave better selectivity of CHOH compared to only Ni (11.2%), which changes from 54.5% to 98% as the ratio changed from 1:1 to 1:5. However, a further increase of the ratio led to a decrease of the selectivity in the reaction time of 5 h. If one takes into account on the product mixture, in the presence of Ni, it could be suggested that hydrolysis and hydrogenation were two reactions to convert DPE. The improved selectivity of CHOH might be considered as a synergistic effect and can be explained by the bifunctional mechanism which required an acid support and a metal function [64]. When the ratio was changed to 1:10, the selectivity of CHOH was dropped to 26%, with an increase in the selectivity of CHPE (74%). In order to verify the influence of reaction time on the 1:10 catalyst, the reaction was extended for 18 h (Fig. 4; marked part). Surprisingly, the conversion was increased to 77.2% and an improved selectivity of CHOH (53.3%) was also detected. It is too early to predict the actual reason behind this observation. Preliminary results of the addition of Ni with Rh/C emerged out as an interesting one for further studies as there are the lot of openings to modify this process to achieve a simple and easy to handle catalyst for the hydrogenolysis of DPE under a mild reaction condition,

4. Conclusion

In conclusion, we have demonstrated a successful application of Rh/C catalyst in the transformation of DPE to monocyclic compounds via hydrogenolysis of C—O bond under a mild reaction condition. In the present reaction condition, the role hydrogen is critical, and could have substantial impact on the cleavage of the C—O bond of DPE. A time course of the reaction based on the hydrogen pressure gave an insight on the reaction pathway. From the beginning of the reaction, a strong influence of hydrogen pressure on the conversion and product distribution was evident. A lower hydrogen pressure was preferable for the rapturing of C—O bond, because of the preferable adsorption of DPE through the C—O bond. Higher hydrogen pressure resulted fully saturated bicyclic products but further hydrogenolysis of the C—O bond of the bicyclic product did not occur under the applied condition. A prominent effect of temperature on the product selectivity suggested that at lower temperature the transformation of DPE was occurred via hydrogenation as higher temperature required for C—O bond cleavage. However, very high temperature again favored hydrogenation because it could affect the solubility of CO_2 in water. Due to the high coverage of the catalyst active site, large excess of substrate also hampered the hydrogenolysis of C—O bond. Studies on different solvents in the neat condition or in the presence of CO_2 and water strongly suggested that a rational choice of the solvents is extremely important part as they affect activity and control the selectivity. Solvents as neat and in the presence of CO_2, mainly produces bicyclic product whereas monocyclic products were detected in the presence of water. A combination catalyst of Rh/C and Ni/MCM-41 was prepared by mixing in different ratios and attempted for this reaction. Interesting preliminary results could serve as the starting point of further systematic studies to achieve better performances on solid catalysts for DPE hydrogenolysis.

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