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An efficient cleavage of the aryl ether C–O bond in supercritical carbon dioxide–water[†]

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A simple and highly efficient Rh/C catalyzed route for the cleavage of the C–O bond of aromatic ether at 80 °C in the presence of 0.5 MPa of H₂ in the scCO₂-water medium is reported; CO₂ pressure and water play a key role under the tested conditions.

Lignocellulosic biomass comprises of cellulose, hemicellulose and lignin and has a huge appeal for production of second generation bio-fuels. Lignin, which takes up $\sim 40\%$ of the lignocellulosic biomass, is a complex structure with strength and stability mainly due to the presence of various kinds of aryl ether bonds. Breaking of the aryl ether C-O bond is a challenging task as the C-O bond is highly stable and typically difficult to activate.¹ In the past few years, several attempts have been made to develop suitable catalysts or processes for the cleavage of the aryl ether bond, and this might be the best strategy for removing oxygenated groups from the aryl ring.² However, it was difficult to achieve desired cleavage of the C-O bond under the typical heterogeneous conditions even after the application of very high pressure and temperature, which resulted in a mixture of several compounds.³ Recently, a remarkable work of Sergeev et al. revealed an interesting strategy to the selective cleavage of the aryl C-O bond using Ni(COD)2 as a homogeneous catalyst in the presence of a specific carbene ligand and NaOBu as a base.⁴ Furthermore, in a new finding by the same group it was suggested that without any additional dative ligand, selective hydrogenolysis of aryl ethers was also possible using a homogeneous catalyst formed in situ from the well-defined soluble nickel precursor Ni(COD)2 or Ni(CH2TMS)2(TMEDA) and a base additive (tBuONa) in m-xylene at 120 °C.4 Following the first development by Sergeev et al., various efforts were made to improve the reaction conditions and efficiency of the Ni catalysts using different reducing agents or reaction media.⁵ From earlier and recent literature, it is evident that Ni-based catalysts (mainly homogeneous) are among the potential candidates with high

efficiency for hydrogenolysis of the C–O bond. However, homogenous catalysts suffer from difficulties in product separation, reusability and are sometimes difficult to handle because of their air sensitivity.⁶ Thus, it was necessary to develop a heterogeneous catalyst for the hydrogenolysis of the aryl C–O linkage, which is easy to handle, and advantageous for large-scale application. In a recent approach, 57 wt% of the Ni/SiO₂ catalyst was used for the cleavage of the aryl ether bond in aqueous media.⁷ The heterogeneous catalytic system required an excessive amount of catalyst or a longer reaction time.

In this work, we attempted to develop a simple and convenient method for the cleavage of the aryl C–O bond. Here, diphenyl ether (DPE) was used as a model compound for hydrogenolysis over 5% Rh/C as a heterogeneous catalyst in a supercritical carbon dioxide (scCO₂)-water system (Scheme 1). The use of a diaryl ether model compound represents a firm test of the catalyst's effectiveness in the cleavage of ether linkages. The reason behind using scCO₂ as the reaction medium was its tunable properties related to high product selectivity, clean product separation as well as non-toxicity and non-flammability. Instead of expensive metal hydrides, molecular H_2 was used as the source of H_2 . In the studied process, activated H_2 breaks the aryl C–O bond at 80 °C within a reaction time of 5 h.

As we targeted the development of simple and practical heterogeneous catalysts, the reaction was conducted over different solid catalysts such as Ni, supported on MCM-41, and noble metals like Pt, Pd and Rh on MCM-41 as well as on activated carbon (C). Among the solid catalysts, activated carbon supported catalysts were previously used for hydrogenolysis of organosolv lignin under harsh reaction conditions.⁸ Table 1 shows the results of catalyst screening for the hydrogenolysis of DPE. Among the MCM-41 supported



Scheme 1 Possible reaction path of DPE hydrogenolysis-hydrogenation.

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Table 1 Catalyst screening for DPE hydrogenolysis-hydrogenation in scCO₂^a

			Product (selectivity (%))					
Entry	Catalyst	Conv. (%)	DCHE	CHPE	СНОН	CH/BZ		
1	Ni/MCM-41	50.1	0.0	78.9	11.2	5.2/4.7		
2	Pt/MCM-41	_	_	_	_	_		
3	Pd/MCM-41	82.3	0.0	90.2	9.8	0.0/0.0		
4	Rh/MCM-41	65.6	0.0	68.4	30.0	1.6/0.0		
5	Pt/C	_			_	_		
6	Pd/C	52.1	0.0	62.7	17.3	11.2/8.8		
7	Rh/C	100.0	0.0	0.0	96.0	2.2/1.8		
8^b	Rh/C	100.0	98.2	0.0	1.8	0.0/0.0		
9 ^c	Rh/C	100.0	0.0	0.0	100.0	0.0/0.0		

^{*a*} Reaction conditions: catalyst:substrate = 1:5, $P_{CO_2} = 10$ Mpa, $P_{H_2} = 0.5$ Mpa, temp. = 80 °C, time = 5 h, water = 4 ml, entries 1–4 were prepared in our laboratory; entries 5–7 are from Aldrich. ^{*b*} Entry 8 = no water. ^{*c*} Entry 9 = phenol as the substrate; DCHE = dicyclohexyl ether; CHPE = cyclohexyl phenyl ether; CH = cyclohexane, BZ = benzene.

catalysts, Pt was inactive, under the condition used (Table 1; entry 2), whereas Ni, Pd and Rh exhibited high conversion from 50 to 80%. However, the main product was partially hydrogenated cyclohexyl phenyl ether (Table 1; entries 1, 3 and 4). As the catalyst support for Pt, Pd and Rh was changed to activated carbon, Pt remained inactive (Table 1; entry 5). Interestingly, Pd and Rh showed impressive results in the formation of the C-O bond cleavage product. In the presence of Pd, DPE was converted to cyclohexyl phenyl ether (62.7%), cyclohexanol (17.3%), cyclohexane (11.2%) and benzene (8.8%) (Table 1; entry 6). On the other hand, DPE was completely converted to mainly cyclohexanol under similar reaction conditions over the Rh/C catalyst (Table 1; entry 7). Thus, depending on the performances, Rh/C was selected as an effective catalyst for hydrogenolysis of the C-O bond of DPE and further used to study the different reaction parameters. The uniqueness in the product selectivity over the Rh catalyst was also observed previously.9

Fig. 1 exhibits the product distribution profile of the reaction with the variation in CO₂ pressure at a fixed temperature of 80 °C. No change in the conversion within the studied range of 7–18 MPa was observed. The result shows a significant effect of CO₂ pressure on product distribution. In the low pressure region (7–12 MPa), cyclohexanol was detected as the major product; however when the pressure was enhanced to >12 MPa, dicyclohexyl ether was formed and reached a selectivity of ~50%. These results implied that the catalytic path for this reaction at lower pressure was distinct from



Fig. 1 Effect of CO₂ pressure on the hydrogenolysis-hydrogenation of DPE; reaction conditions: $P_{H_2} = 0.5$ Mpa; catalyst: substrate = 1:5; temp. = 80 °C; time = 5 h; water = 4 ml.

the path at higher pressure. In the lower pressure region hydrogenolysis of DPE was favoured, which results mainly in cyclohexanol and the possible source of cyclohexanol was phenol. To confirm this process, a separate experiment was conducted using phenol under similar working conditions, in which phenol was successfully converted to cyclohexanol (Table 1; entry 9). No direct hydrogenolysis from phenol or benzene or cyclohexanol to cyclohexane was detected. In the higher pressure region the formation of dicyclohexyl ether might be expected from the dehydrogenation or condensation (dehydration) of cyclohexanol or hydrogenation of DPE. Under the studied reaction conditions, we can neglect the first two options, thus, hydrogenation of DPE might be the possible route for generation of dicyclohexyl ether. At higher pressure, DPE was highly soluble in scCO₂ (Fig. S1, ESI⁺). Hence, a large amount of H₂ would be available in the medium, which easily hydrogenated DPE to dicyclohexyl ether. The hydrogenation of DPE to dicyclohexyl ether required higher H₂ pressure over the Rh/C catalyst.¹⁰ To explore the specific contribution of the individual medium, the reaction was carried out separately in CO2 and in water. In CO2, DPE was completely converted to dicyclohexyl ether (98%) and cyclohexanol (2%) (Table 1; entry 8). Similarly, in water the conversion of DPE dropped sharply to $\sim 15\%$ with the formation of dicyclohexyl ether (68%), cyclohexanol (22.5%) and cyclohexane (9.5%) (see Table S1, entry 1 (ESI[†])). Hence, hydrogenation of the aromatic ring without any cleavage of the C-O bond was the major process, when CO2 and water were used independently. Therefore, a combined effect of water and scCO2 as the biphasic medium was necessary for hydrogenolysis of DPE because CO2 helps to accelerate the process and water dominates the hydrogenolysis over hydrogenation at lower pressure. It is too early to predict the exact route for this reaction as study of the reaction mechanism is still underway.

From the accumulated results, one can understand that water played an important role. Keeping the other reaction parameters fixed, the amount of water was varied from 0 to 4 ml. We have found that the conversion of DPE remained unaffected in the presence or absence of water. In any case 100% conversion was observed. However, there was a strong correlation between the product distribution and the amount of water used (see Fig. S2, ESI⁺). As mentioned before, in the absence of water, mainly dicyclohexyl ether was formed. Surprisingly, when the same reaction was performed with the addition of 0.5 ml of water along with CO₂, the selectivity to cyclohexanol was increased to 32% and finally reached the highest selectivity of 96% when the amount of water was 4 ml within the reaction time of just 5 h. Thus, an optimum amount of 4 ml water was used throughout the reaction. The increasing selectivity of cyclohexanol did not result from dicyclohexyl ether because it was inactive under the tested conditions.

Regarding the effect of H_2 pressure, no reaction occurred in the absence of H_2 . Thus, H_2 was introduced into the system and the pressure was changed from 0.1 to 1.5 MPa. As a result, the conversion of DPE was enhanced from 38.2% to 100% when the pressure increased from 0.1 to 0.5 MPa, and the detected product was mainly cyclohexanol. However, higher H_2 pressure (>0.5 MPa) accelerated the reaction with dicyclohexyl ether as a major product and confirmed the origin of dicyclohexyl ether at higher pressure of CO₂. The most significant point for this system was the potential to control the formation of a C–O bond

Table 2Hydrogenolysis-hydrogenation of different aryls and aryl alkyl ethers^aas represented in Scheme 2

			Selectivity (%)				
Entry	Substrate	Conv. (%)	2(6)	3(7)	4(8)	5(9)	
1		100	42.1	(57.9)	0.0	0.0	
2		85.2	48.2	(38.6)	(8.9)	(7.3)	
3	F OH	87.3	46.2	(50.1)	(1.2)	(2.5)	
4	H ₂ N	22.1	1.1	1.3	(55.9)	(41.7)	
5 ^{<i>b</i>}		100	(49.9)	(48.6)	0.0	0.0	
6		60.2	(100)	_	_	_	
7		52.1	(100)	_	_	_	
8		55.5	(100)	_	_	_	

^{*a*} Reaction conditions: catalyst: substrate = 1:5, $P_{CO_2} = 10$ Mpa, $P_{H_2} = 0.5$ Mpa, temp. = 80 °C, water = 4 ml; reaction time: entry 1 = 5 h, entry 2 = 12 h; entry 3–8 = 18 h; "—" = not determined. ^{*b*} 6 = cyclohexylmethanol.



cleavage product or an aromatic ring hydrogenation product without any cleavage by simply tuning the reaction parameters.

After finding primary reaction conditions, we applied this method to other aryl ether compounds with different substitution patterns and the results are shown in Table 2. The results show that the developed method was applicable for C–O bond cleavage of unsymmetrical aryl ethers and alkyl aryl ethers. Depending on the nature of the substrate, conversion varied from 20–100%. The reaction of symmetrical aryl ether was faster and produced corresponding hydrogenated arene and phenol compounds (Table 2; entry 1). On the other hand, unsymmetrical aryl ether bearing either electron withdrawing or electron donating groups or both required a longer reaction time for the cleavage (Table 2; entries 2–4). In terms of product selectivity, an apparent

correlation was observed depending on the presence of electron withdrawing and electron donating groups, which dictated the formation of saturated or unsaturated alcohol or arene compounds. In addition, the cleavage of the C–O bond of alkyl aryl ether compounds was also achieved successfully (Table 2; entries 6–8).

For this system, instead of scCO₂, different organic solvents such as methanol, ethanol, isopropanol, tetrahydrofuran and hexane were used along with water (see Table S1, ESI⁺). According to the results, highest and lowest conversion of DPE was detected in hexane (100%) and methanol (47%), respectively. In addition, depending on the solvent used, product distribution was changed. In isopropanol, the highest selectivity of cyclohexanol (92%) was observed but the selectivity of dicyclohexyl ether was very high about 70% when hexane was used. The selectivity of cyclohexanol follows the order of isopropanol > ethanol > methanol > tetrahydrofuran > hexane. No definite trend of solvent polarity was detected in the catalytic performances, but it could be stated that the reaction was faster in non-polar solvents, which preferred hydrogenation rather than hydrogenolysis. A strong role of the solvent was reported before as they affected the activity and selectivity of the reaction using the RANEY[®] Ni catalyst.¹¹ It should be mentioned that although scCO₂ is considered as a non-polar solvent, it is superior to similar organic solvents as it possesses substantially different characteristics, which can direct the activity and selectivity of a reaction. Recycling of the catalyst confirmed its stability (see Table 1, entries 7 and 8; ESI⁺).

In conclusion, we have developed a simple and highly reactive catalytic system for the cleavage of the aryl ether bond of DPE. Under the mild reaction conditions, it was possible to achieve very high catalytic performance. The studied method was also extended to different types of symmetrical and unsymmetrical aryl and alkyl aryl ether compounds. Future work will be directed to the mechanistic aspects to understand the actual process for large-scale applications.

Notes and references

- 1 E. Furimsky, Appl. Catal., 2000, 199, 147.
- P. Á. Bercedo and R. Martin, J. Am. Chem. Soc., 2010, 132, 17352;
 A. Maercker, Angew. Chem., Int. Ed. Engl., 1987, 26, 972; P. Dabo,
 A. Cyr, J. Lessard, L. Brossard and H. Ménard, Can. J. Chem., 1989, 77, 1225; M. Tobisu, K. Yamakawa, T. Shimasaki and N. Chatani, Chem. Commun., 2011, 47, 2946.
- 3 J. Shabtai, N. K. Nag and F. E. Massoth, J. Catal., 1987, 104, 413.
- 4 A. G. Sergeev and J. F. Hartwig, *Science*, 2011, 332, 439; A. G. Sergeev,
 J. D. Webb and J. F. Hartwig, *J. Am. Chem. Soc.*, 2012, 134, 20226.
- 5 B. S. Samant and G. W. Kabalka, *Chem. Commun.*, 2012, 48, 8658;
 M. Tobisu and N. Chatani, *ChemCatChem*, 2011, 3, 1410; P. Kelley,
 S. Lin, G. Edouard, M. W. Day and T. Agapie, *J. Am. Chem. Soc.*, 2012, 134, 5480.
- 6 J. S. Miller and K. L. Pokhodnya, J. Mater. Chem., 2007, 17, 3585.
- 7 J. He, C. Zhao and J. A. Lercher, J. Am. Chem. Soc., 2012, 134, 20768.
- 8 M. Nagy, K. David, G. J. P. Britovsek and A. J. Ragauskas, *Holz-forschung*, 2009, **63**, 513; N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626; N. Yan, Y. A. Yuan, R. Dykeman, Y. A. Kou and P. J. Dyson, *Angew. Chem., Int. Ed.*, 2010, **49**, 5549.
- 9 M. Chatterjee, H. Kawanami, T. Ishizaka, M. Sato, T. Suzuki and A. Suzuki, *Catal. Sci. Technol.*, 2011, 1, 1466.
- 10 P. N. Rylander and M. Kilroy, Engelhard Ind. Tech. Bull., 1968, 9, 14.
- 11 X. Wang and R. Rinaldi, ChemSusChem, 2012, 5, 1455.