

# Selective hydrogenation of unsaturated aldehydes in a poly(ethylene glycol)/compressed carbon dioxide biphasic system

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Hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes (citral, 3-methyl-2-butenal, cinnamaldehyde) has been studied with tetrakis(triphenylphosphine) ruthenium dihydride ( $\text{H}_2\text{Ru}(\text{TPP})_4$ ) catalyst in a poly(ethylene glycol) (PEG)/compressed carbon dioxide biphasic system. The hydrogenation reaction was slow under PEG/ $\text{H}_2$  biphasic conditions at  $\text{H}_2$  4 MPa in the absence of  $\text{CO}_2$ . When the reaction mixture was pressurized by a non-reactant of  $\text{CO}_2$ , however, the reaction was significantly accelerated. As  $\text{CO}_2$  pressure was raised from 6 MPa to 12 MPa, the conversion of citral increased from 35% to 98%, and a high selectivity to unsaturated alcohols (geraniol and nerol) of 98% was obtained. The products were able to be extracted by high pressure  $\text{CO}_2$  stream and separated from the PEG phase, dissolving the Ru complex catalyst and the catalyst was recyclable without any post-treatment.

## Introduction

Selective hydrogenation of unsaturated aldehydes is an important step in producing unsaturated alcohols, which are important intermediates in the synthesis of fine chemicals like flavor, fragrance and pharmaceutical compounds.<sup>1</sup> However, since the  $\text{C}=\text{C}$  bond is more easily hydrogenated than the  $\text{C}=\text{O}$  bond, the selective hydrogenation of  $\text{C}=\text{O}$  in the aldehyde molecules with a conjugated  $\text{C}=\text{C}$  is still a challenging task. Many attempts have been made to develop suitable catalytic systems for improving the selectivity to unsaturated alcohols. Organometallic catalysts<sup>2</sup> have attracted continuous interest due to their high activity and selectivity and extensive studies have been carried out using Ru, Rh, Ir and other metals with phosphine or phosphate ligands.<sup>3–5</sup> However, the difficulties in the separation of the noble metals and the ligands, which are often very expensive and/or toxic, have hindered their use in industry.

The immobilization of homogeneous catalysts was proposed to resolve the above problems, and for organometallic complex catalysts, they are usually immobilized in water,<sup>6–8</sup> ionic liquid,<sup>9</sup> fluorous liquid<sup>10</sup> or ethylene glycol<sup>11</sup> and the reactants and products are usually contained in organic phase. In the water–organic system, the catalysts must be modified to be sufficiently soluble in water, and the activity and/or selectivity of the water-soluble catalysts are normally lower than those of the organo-soluble parent catalysts. In the case of ionic liquids, the hydrophobic catalysts could be used and recycled easily.<sup>12,13</sup> However, most of

ionic liquids are expensive and knowledge of their environmental impacts is still limited. Recently, poly(ethylene glycol) (PEG) has attracted increasing interest because it is non-volatile, recyclable and stable to acid and base.<sup>14–16</sup> In addition, it can dissolve many organometallic complex catalysts without any modification of their structures,<sup>17</sup> and it is inexpensive and non-toxic. In 1995, PEG was firstly used for the immobilization of homogeneous catalysts.<sup>18</sup> It was reported that a water-soluble catalyst of  $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$  was dissolved in a PEG film and the mixture was dispersed on a silica gel; this supported liquid phase catalyst (SLPC) was effective for hydroformylation of 1-hexene. Then, the SLPCs were studied in various organic chemical reactions and have been well reviewed in the literature.<sup>19</sup> Recently, PEG and compressed carbon dioxide have been investigated as recyclable and environmentally benign solvents in chemical reactions such as the Heck reaction, hydrogenation, hydroformylation, Suzuki cross-coupling and epoxidation.<sup>20–28</sup> However, compressed carbon dioxide's low ability to dissolve organometallic complexes prevents its utilization in homogeneous catalytic synthesis. In contrast, PEG can dissolve various metal complexes and it can also dissolve large amount of  $\text{CO}_2$  at high pressure, forming an expanded-liquid phase. Such an expansion causes changes in the physical properties of the PEG– $\text{CO}_2$  liquid mixture, lowering melting points and viscosity<sup>29</sup> and increasing gas/liquid diffusion rates<sup>30</sup> and ability to dissolve  $\text{H}_2$ .<sup>31</sup> Furthermore, PEG has a very limited solubility in compressed carbon dioxide and thus the organometallic catalysts could be immobilized in the PEG phase, useable for chemical reactions, and recyclable. When soluble organometallic complexes are used in the presence of pressurized  $\text{CO}_2$ , the catalytic reactions occur in the  $\text{CO}_2$ –expanded PEG phase. Heldebrandt and Jessop<sup>32</sup> studied the hydrogenation of styrene catalysed with Wilkinson's complex  $\text{RhCl}(\text{Ph}_3\text{P})_3$  in compressed  $\text{CO}_2$ /PEG system. They pointed out that the catalyst remained stable in the PEG medium and could be recycled four times

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without noticeable loss of activity after the product, ethylbenzene, was separated by compressed carbon dioxide extraction. Leitner and co-workers<sup>33,34</sup> reported that aerobic oxidation of alcohols could be catalysed effectively by PEG-stabilized palladium nanoparticles in compressed CO<sub>2</sub>/PEG system. Recently, Wang *et al.*<sup>35</sup> also showed that aerobic oxidation of styrene catalysed by PdCl<sub>2</sub>/CuCl could occur smoothly in compressed CO<sub>2</sub>/PEG system.

Those results indicate that compressed CO<sub>2</sub>/PEG biphasic systems are an attractive reaction medium, and so it is interesting and significant to further study their applications to recyclable and green multiphase catalytic systems for various reactions. The present work has hence been undertaken to investigate the features of compressed CO<sub>2</sub>/PEG biphasic systems for selective hydrogenations of  $\alpha,\beta$ -unsaturated aldehydes with a catalyst of H<sub>2</sub>Ru(TPP)<sub>4</sub>. For comparison, the same hydrogenation reactions were conducted in homogeneous systems using either cyclohexane or compressed carbon dioxide as a solvent. The effects of CO<sub>2</sub> pressure and molecular weight of PEG on the selective hydrogenation and the separation and recyclability of the catalyst-containing PEG phase were examined in detail.









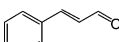
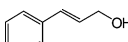
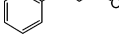

## Results and discussion

Three  $\alpha,\beta$ -unsaturated aldehydes were hydrogenated using a biphasic system of gas (H<sub>2</sub>, CO<sub>2</sub>) and liquid (PEG) including H<sub>2</sub>Ru(TPP)<sub>4</sub> complex catalyst. Table 1 shows that for all the alde-

hydes examined, the C=O bonds are selectively hydrogenated, giving the corresponding unsaturated alcohols with selectivity levels >95%. These high selectivity values for unsaturated alcohols are comparable to the best data reported for similar hydrogenation reactions in water–toluene biphasic systems using water-soluble Ru-TPPTS and Ir-TPPTS catalysts.<sup>36</sup> The conversion levels with 3-methyl-2-butenal and citral are larger than that with cinnamaldehyde, probably due to differences in the structure of groups attached to the  $\gamma$ -carbon. The phenyl group is less electron-donating and can conjugate with the unsaturated bonds, which would make the C=O bond of cinnamaldehyde less reactive compared with the other two aldehydes.

The influence of solvents and CO<sub>2</sub> pressure has been examined using citral as a model substrate. It is well known that the rate of hydrogenation reactions depends on the solvents used.<sup>3,37,38</sup> Table 2 shows the results of citral hydrogenation runs with H<sub>2</sub>Ru(TPP)<sub>4</sub> catalyst in different solvents. In a conventional non-polar organic solvent of cyclohexane, a total conversion of 75% was observed with a selectivity of 93% to unsaturated alcohols (entry 1). A PEG (PEG-1000) solvent gave a lower conversion of 51% with a comparable high selectivity of 98% (entry 2). This difference in the total conversion between cyclohexane and PEG may be ascribable to differences in the solvent natures, which affect the solubility of a gaseous reactant of H<sub>2</sub> in the liquid phase and the rate of mass transfer between the gas and liquid phases and/or in the liquid phase. The viscosity of liquid PEG is known to drop dramatically (8–10-fold) by dissolution of CO<sub>2</sub>.<sup>39</sup>

**Table 1** Results of hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with H<sub>2</sub>Ru(TPP)<sub>4</sub> in compressed CO<sub>2</sub>/PEG

Entry	Substrate	Product	Time/h	Conversion (%)	Selectivity (%)
1			0.5	82	98
2			1	100	95
3			1	87	97
4			1.5	>99	99
5			2	43	95
6			8	>99	98

Reaction conditions:  $\alpha,\beta$ -unsaturated aldehydes 2 mmol, H<sub>2</sub>Ru(TPP)<sub>4</sub> 0.01 mmol; PEG-1000 2 g, H<sub>2</sub> 4 MPa, CO<sub>2</sub> 10 MPa, 338 K.

**Table 2** Results of hydrogenation of citral with H<sub>2</sub>Ru(TPP)<sub>4</sub> in different solvents

Entry	Solvent	Conversion (%)	Selectivity (%)	
			Citronellol	Geraniol & nerol
1	Cyclohexane	75	4	93
2	PEG-1000	51	2	98
3	CO <sub>2</sub>	100	1	99
4	CO <sub>2</sub> /cyclohexane	96	1	99
5	CO <sub>2</sub> /PEG600	100	1	99
6	CO <sub>2</sub> /PEG-1000	100	1	99
7	CO <sub>2</sub> /PEG2000	100	1	99
8	CO <sub>2</sub> /PEG6000	100	1	99
9	CO <sub>2</sub> /PEG-10000	79	1	99
10	CO <sub>2</sub> /PEG-12000	52	1	99

Reaction conditions: citral 2 mmol, H<sub>2</sub>Ru(TPP)<sub>4</sub> 0.01 mmol, cyclohexane 2 ml, PEG 2 g, CO<sub>2</sub> 8 MPa, H<sub>2</sub> 4 MPa, 338 K, 2 h.

Probably the solubility of  $H_2$  and the rate of mass transfer should be larger in cyclohexane than in PEG. When neat 8 MPa  $CO_2$  was used, a higher conversion and a similar high selectivity were obtained (entry 3). The reactant of citral used was completely soluble in the solvent,  $CO_2$ , and the catalyst was also almost soluble (a minor quantity of the catalyst loaded was not soluble, as seen by visual observation). Under the present conditions, therefore, the hydrogenation should occur in the homogeneous  $CO_2$  gas phase, in which gas–liquid mass transfer boundary is absent and  $H_2$  can be completely miscible, resulting in the high conversion as compared with those obtained in cyclohexane and PEG-1000. The specific nature of the complex catalyst to the selective hydrogenation of carbonyl bond does appear in the compressed  $CO_2$  gas phase as well.

It is interesting that, when the biphasic reaction mixtures using cyclohexane and PEG were pressurized by 8 MPa  $CO_2$ , the conversion was enhanced to levels > 95% and the selectivity to unsaturated alcohols was almost perfect (99%) (entries 4, 5). The pressurization with  $CO_2$  promotes the dissolution of  $H_2$  into the liquid phases and the mass transfer in the liquid reaction phases, which may explain the rate enhancement observed. The liquid phases dissolving  $CO_2$  molecules are also effective media for the  $H_2Ru(TPP)_4$  complex catalyst to show its specific activity for selective hydrogenation of the C=O bond. A slight increase in the selectivity was observed with cyclohexane (entries 1, 4) and this could indicate the significance of molecular interactions between the carbonyl bond and the dissolved  $CO_2$  molecules for the selectivity enhancement.<sup>40–42</sup>

In addition, PEG solvents with different molecular weights have been tested for citral hydrogenation under biphasic conditions with 8 MPa  $CO_2$ . Table 2 indicates that the PEG solvents of 600–6000 in molecular weight show no differences in the conversion and in the selectivity (entries 5–8). However, when the molecular weight is increased to 10 000 and 12 000, the conversion decreases to 79% and 52%, respectively, but the selectivity to unsaturated alcohols remains unchanged (entries 9, 10). Their more viscous natures may have negative effects on the dissolution of  $H_2$  and the mass transfer in the liquid reaction phase.

Table 3 gives the results of citral hydrogenation runs at different  $CO_2$  pressures with a solvent of PEG-1000. The reaction mixture was biphasic at pressures up to 16 MPa, as confirmed by visual observations. The solvent was observed to expand by dissolution of  $CO_2$  with increasing pressure but to a

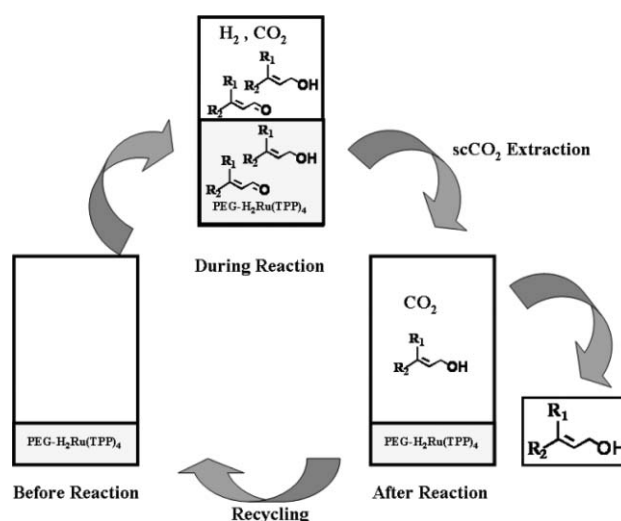
**Table 3** Influence of  $CO_2$  pressure on hydrogenation of citral with  $H_2Ru(TPP)_4$  in compressed  $CO_2$ /PEG

Entry	$CO_2$ /MPa	Conversion (%)	Selectivity (%)	
			Citronellol	Geraniol & nerol
1	0	13	3	97
2	6	35	3	97
3	8	53	2	98
4	10	87	3	97
5	12	98	2	98
6	14	100	2	98
7	16	100	1	99

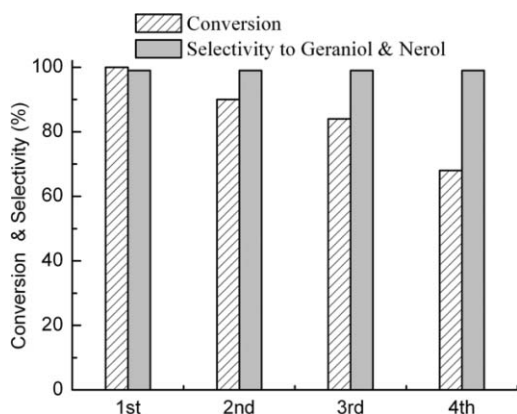
Reaction conditions: citral 2 mmol,  $H_2Ru(TPP)_4$  0.01 mmol, PEG-1000 2 g,  $H_2$  4 MPa, 338 K, 1 h.

less extent <10%, in contrast to a conventional organic solvent like cyclohexane.<sup>16</sup> In the absence of  $CO_2$ , a low conversion of 13% was obtained under the conditions used but the selectivity to unsaturated alcohol was as high as 97%, owing to the specific catalytic feature of the  $H_2Ru(TPP)_4$  complex. It should be noted that the conversion can significantly be enhanced when high  $CO_2$  pressure is used. At 12 MPa or higher, the hydrogenation is completed in 1 h. It is reported in the literature that in aerobic oxidation of styrene with  $PdCl_2/CuCl$  catalyst in the  $scCO_2$ /PEG biphasic system,  $CO_2$  pressure has a small effect on the rate of oxidation but a larger effect on the product selectivity.<sup>35</sup>

The recyclability of  $H_2Ru(TPP)_4$  complex catalyst has been examined for citral hydrogenation under  $CO_2$  gas-PEG liquid biphasic conditions. Scheme 1 illustrates the processes of catalytic reaction and catalyst–product separation. The products were extracted and separated from the PEG phase with compressed carbon dioxide. After reaction, the reaction mixture was kept in contact with a stream of 10 MPa  $CO_2$  at a flow rate of  $5\text{ cm}^3\text{ min}^{-1}$  and at 323 K until no products were detected in the effusion from the reactor and collected in *n*-hexane. Then, the separated PEG phase containing the complex catalyst was used for next reaction run without further purification or activation. Fig. 1 shows the results of four runs (three recycling runs), indicating that the conversion decreases but the high selectivity to unsaturated alcohols (geraniol and nerol) remains unchanged. A possible factor responsible for the decrease in the catalytic activity observed is the structural change of  $H_2Ru(TPP)_4$  complex catalyst. We observed a change of the PEG liquid phase from yellow to olive in color after recycling runs.<sup>43,44</sup> This suggests the dissociation and/or partial oxidation of the phosphine ligands, causing some change of the catalyst complex molecules and resulting in the decrease in the catalytic activity. From the point of industrial utilization, a more air-stable catalyst should be desired and investigated in further work. Another possibility for the loss of activity is the leaching of Ru species. As described above, the products were extracted by  $scCO_2$  and collected in *n*-hexane. The concentration



**Scheme 1** Reaction, separation, and recycling processes in hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with Ru complex catalyst under gas ( $H_2$ ,  $CO_2$ )–liquid (PEG) biphasic conditions.



**Fig. 1** Results of catalyst recycling test in hydrogenation of citral with  $\text{H}_2\text{Ru}(\text{TPP})_4$  in compressed  $\text{CO}_2$ /PEG. Reaction conditions: citral 2 mmol,  $\text{H}_2\text{Ru}(\text{TPP})_4$  0.01 mmol, PEG-1000 2 g,  $\text{H}_2$  4 MPa,  $\text{CO}_2$  8 MPa, 338 K, 2 h.

of Ru species collected in the *n*-hexane was measured by atomic absorption spectroscopy, which was 0.0065 ppm. This indicates that the leaching of Ru species is less than 0.001% of the initial amount of Ru loaded in PEG phase; namely,  $\text{H}_2\text{Ru}(\text{TPP})_4$  catalyst could be successfully immobilized in PEG phase and separated from the products easily by  $\text{CO}_2$  extraction. The authors did not measure the quantity of the phosphorous species in the effluent and do not deny the possibility of the leaching and loss of the ligand components as a factor causing the catalyst deactivation observed (Fig. 1). By contrast, the metal leaching was claimed to be responsible for the loss of catalytic activity in the hydrogenation of  $\text{scCO}_2$  in the presence of dimethylamine with  $\text{H}_2\text{Ru}(\text{TPP})_4$  catalyst attached to the terminus of polymer chains.<sup>43</sup>

## Conclusions

The present results demonstrate that the biphasic system of PEG and compressed carbon dioxide is effective for selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes using PEG-soluble  $\text{H}_2\text{Ru}(\text{TPP})_4$  catalyst and  $\text{H}_2$  as a reductant. The reactions can proceed smoothly in this  $\text{CO}_2$ -dissolved expanded liquid PEG phase, in which the solubility of  $\text{H}_2$  is larger and the mass transfer rate is also larger as compared with the viscous neat PEG phase. The organic products are separable from the PEG phase by extraction with high pressure  $\text{CO}_2$  stream and this  $\text{CO}_2$  extraction causes no leaching of Ru species from the PEG phase. The catalyst-containing PEG phase is recyclable without any post-treatment but the activity of the catalyst gradually decreases during the repeated reaction runs, probably due to its structural alteration as indicated by the color change. The high selectivity to unsaturated alcohols can remain unchanged during recycling, which is characteristic of the active form of  $\text{H}_2\text{Ru}(\text{TPP})_4$ .

## Experimental

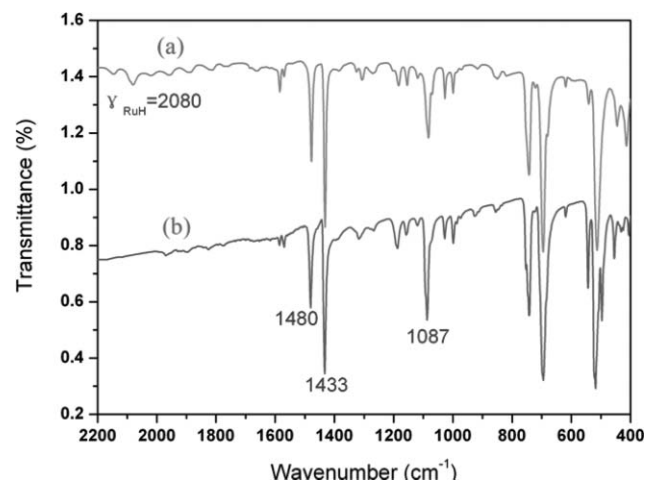
### Chemicals

All experiments were carried out under nitrogen atmosphere. Unsaturated aldehydes,  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , and triphenylphosphine

(TPP) were purchased from Aldrich and PEGs from Beijing Chemical Reagent Company, and they were used without further purification. Gases of  $\text{CO}_2$  (99.995%) and  $\text{H}_2$  (99.999%) (Changchun Xinxing Gas Company) were used as delivered. Benzene and methanol were used in catalyst preparation and cyclohexane in hydrogenation, which were dried and distilled under nitrogen atmosphere before use.

### Catalyst synthesis and characterization

$\text{RuCl}_2(\text{TPP})_3$  and  $(\text{H})_2\text{Ru}(\text{TPP})_4$  were prepared according to the literature.<sup>45,44</sup>  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.8 g, 3.8 mmol) was dissolved in methanol (250 ml) and the solution was refluxed under nitrogen atmosphere at 338 K for 5 min. After cooling, TPP (6.0 g, 22.9 mmol) was added in a TPP/Ru mole ratio of 6, and the solution was refluxed again under nitrogen for 5 h. The complex precipitated from the hot solution and, after cooling, it formed a shiny black crystal. The crystals formed were filtered and washed several times with degassed methanol. Finally, the crystal samples were dried under vacuum. Those crystals were subjected to FTIR measurement with a Bruker Vertex 70 model and absorption bands were observed at 1480, 1433, 1087  $\text{cm}^{-1}$ , as shown in Fig. 2, indicating the formation of  $\text{RuCl}_2(\text{TPP})_3$ . Then,  $(\text{H})_2\text{Ru}(\text{TPP})_4$  was synthesized from this prepared complex.<sup>44</sup>  $\text{Ru}(\text{Cl})_2(\text{TPP})_3$  (1.0 g) was dissolved in a hydrogen-saturated solution of benzene (60 ml)–methanol (100 ml) mixture containing TPP (6.0 g), and then  $\text{NaBH}_4$  was added until the color of the solution changed from deep red to light orange. The solution was stirred for 1 h at room temperature; initially white  $(\text{H})_4\text{Ru}(\text{TPP})_3$  precipitated and changed to yellow  $(\text{H})_2\text{Ru}(\text{TPP})_4$ . The complex formed was filtrated and washed several times with degassed methanol, and then dried at 313 K in vacuum for 12 h. The complex samples prepared were stored under argon before use. The formation of  $(\text{H})_2\text{Ru}(\text{TPP})_4$  complex was confirmed by FTIR (Fig. 2b).



**Fig. 2** FTIR spectra of Ru complex samples prepared: (a)  $\text{H}_2\text{Ru}(\text{TPP})_4$  and (b)  $\text{RuCl}_2(\text{TPP})_3$ .

### Hydrogenation reaction

The hydrogenations were carried out in a stainless steel batch reactor (50 ml).  $(\text{H})_2\text{Ru}(\text{TPP})_4$  (0.01 mmol), PEG (2 g) and



reactant (2 mmol) were loaded into the reactor quickly and then the reactor was sealed and flushed with 2 MPa CO<sub>2</sub> more than three times. After the reactor was heated up to a reaction temperature of 338 K, first H<sub>2</sub> and then CO<sub>2</sub> were introduced into the reactor up to the desired pressures with a high-pressure liquid pump. The reaction time was recorded after the stirring was started. After reaction, the reactor was cooled down to room temperature and depressurized carefully by a backpressure regulator. Then, the products were extracted with *n*-hexane or compressed carbon dioxide and analysed with gas chromatography (GC-Shimadzu-14C, FID, Capillary column Rtx-Wax 30 m, 0.53 mm, 0.25 mm) and gas chromatography/mass spectrometry (GC/MS, Agilent 5890). The extraction with compressed carbon dioxide was made by passing 10 MPa CO<sub>2</sub> through the reactor at a flow rate of 5 ml min<sup>-1</sup> and at 323 K until no products were detected in effusion.

### Phase behavior studies

Since the phase behavior plays a very important role for the chemical reactions in compressed carbon dioxide, it is crucial to observe the state of the reaction system. An 80 ml high-pressure sapphire-windowed reactor was used to examine the phase behavior. Appropriate amounts of reactants, PEG and (H)<sub>2</sub>Ru(TPP)<sub>4</sub> were added into the reactor in order to create the same conditions as used in the 50 ml reactor for hydrogenation runs, and then the system was flushed with 2 MPa CO<sub>2</sub> more than three times. The reactor was heated up to 338 K (reaction temperature) and H<sub>2</sub> (4.0 MPa) was introduced into the reactor and then CO<sub>2</sub> was added gradually up to the desired total pressure ranging from 4 to 21.0 MPa. The mixture was maintained at a certain pressure for several minutes while stirring. Then the stirring was stopped and the state of mixture was observed by the naked eye from the window, as described previously.<sup>46</sup>

### Acknowledgements

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