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Aromatic hydrogenation of benzyl alcohol and its derivatives using compressed CO_2 /water as the solvent⁺

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A green approach to the aromatic hydrogenation of benzyl alcohol and its derivatives to produce cyclohexanemethanol was demonstrated in this report. In this work, the hydrogenation reactions were carried using neat, CO₂-expanded liquid (CXL), water and compressed CO₂/water, as the solvents. It was found out that using water as the solvent achieved the highest yield of the hydrogenation product (>96%). On the other hand, using the compressed CO₂/water system as the solvent significantly enhanced the reaction rate (only 1/5 of the reaction time needed for total conversion when compared to reactions in water) while still maintained high product yield (>90%). It is believed that CO₂ molecules dissolved in water could form carbonic acid simultaneously and the acid was proved to act as a promoter throughout the reaction.

Introduction

There are widespread applications of hydrogenated aromatic compounds in day-to-day life. Aromatic hydrogenation is arguably the most difficult type of hydrogenation due to the need to overcome the high resonance energy of the benzene ring. To our interest, cyclohexanemethanol, that can be made by hydrogenation of benzyl alcohol, and its derivatives have been widely used as an intermediate in pharmaceutical drugs manufacturing. Takagi et al. focused on the catalytic effects during the hydrogenation of several benzyl compounds, which could easily undergo hydrogenolysis reaction.² Their results showed that the yield of cyclohexanemethanol was 81% in ethanol at nearly 373 K, using Ru oxide as the catalyst. Furthermore, Nishimura and Hama reported the main hydrogenation products of benzyl alcohol.³ Their research showed that Rh catalysts could have been poisoned due to the formation of the byproduct, cyclohexanecarboxaldehyde. However, this product was not observed when using Pt catalysts. Until now, there is little information regarding using green solvents for the aromatic hydrogenation reactions. Nowadays, the use of organic solvents has been seriously evaluated due to the principle of searching for green solvents.4 Traditional organic solvents could have several drawbacks that could not meet the modern day standards, such as being volatile, flammable, explosive, harmful to the environment and toxic to the human being. Therefore, it is necessary to find out some alternative media that can avoid these shortcomings. Recently, water⁵ and supercritical fluids (SCF)⁶ and their uses as

solvents in chemical reactions, including hydrogenation, have been explored in several studies. The advantages of using water as the solvent are well known. In brief, water is a green and abundant natural resource, which can be easily obtained. Maegawa et al. reported the hydrogenation of a variety of aromatics, using transition-metal heterogeneous catalysts in water under mild conditions.^{5a} The results showed the possibilities of aromatics hydrogenation in water, which were successfully demonstrated by numerous examples. On the other hand, the applications of SCF have gradually been the object of study over the past few decades owing to the unique physical properties of supercritical fluids, especially supercritical carbon dioxide (scCO₂). Seki et al. reviewed the heterogeneous catalytic hydrogenation of organic compounds processed by SCF.^{6b} In the review paper and several other recent articles, a number of examples of applying CO₂, including scCO₂ and CO₂-expanded liquid (CXL), as a substitute for conventional organic solvents were listed.⁷ Comparing to the conventional organic solvents, scCO₂ is miscible with hydrogen gas, leading to a reduction of the interfacial mass transfer resistance between gas and liquid. In addition, scCO₂ has long been considered as a green solvent because of its non-toxic, non-flammable and environmental friendly properties. Zhao and Arai's groups had proposed the mechanism of the hydrogenation of nitro and nitroso compounds in scCO₂ and conventional solvents.⁸ One of their works showed that using scCO₂ as the solvent was more suitable than using ethanol for the hydrogenation of chloronitrobenzene, due to the suppressing dehalogenation by the addition of CO2.8b In addition, the feasibility of the hydrogenation of nitrobenzene and its derivatives in compressed CO2/water system was also reported. Their latest study pointed out that using compressed CO₂/water as the solvent was more efficient for the hydrogenation of nitrobenzene and chloronitrobenzene.8c In other research by Gao and Li, the addition of CO₂ was influential to the

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hydrogenation of nitrate ions in drinking water.⁹ Thus, to discover more extended examples of using green solvents for aromatic hydrogenation is the primary goal in this study. Therefore, the superiority of several green solvents, including water, CXL and compressed CO₂/water was investigated for the hydrogenation of benzyl alcohol and its derivatives. A self-synthesized silica-supported Ru catalyst (Ru/MCM-41) using chemical fluid deposition technique was selected in this study. A comparison in catalyst efficiency between the self-synthesized Ru/MCM-41 catalyst and a commercial active carbon-supported Ru catalyst (Ru/C) was also made in this work.

Results and discussion

Hydrogenation of benzyl alcohol

Scheme 1 shows the reaction pathway of the benzyl alcohol hydrogenation, which yielded toluene, methylcyclohexane, cyclohexenemethanol and cyclohexanemethanol as the main products. Cyclohexenemethanol was detected by GC-MS. It is speculated that 1-cyclohexene-1-methanol is the major component of the three positional isomers of cyclohexenemethanol since it is more stable than the other two isomers, 2-cyclohexene-1-methanol and 3-cyclohexene-1-methanol. Moreover, an undesirable byproduct, cyclohexanecarboxaldehyde, was always detected less than 0.1% in this study and, therefore, neglected during the product selectivity calculation. Table 1 shows the comparison between Ru/C and Ru/MCM-41 in hydrogenation of benzyl alcohol at 323 K. In order to obtain high selectivity of cyclohexanemethanol, a complete reaction was preferred. In the preliminary test, it was found out that the selectivity towards toluene and methylcyclohexane was increased with increasing reaction temperature. However, the selectivity of the fully hydrogenated product cyclohexanemethanol was poor. Therefore, the reaction temperature was adjusted to a lower temperature in order

Scheme 1 Reaction pathway of the benzyl alcohol hydrogenation. 1: benzyl alcohol, 2: toluene, 3: methylcyclohexane, 4: cyclohexenemethanol, 5: cyclohexanemethanol.

	Catalyst ^b	Conv. (%)	Product selectivity (%)					
Entry			2	3	4	5	Yield ^c (%)	
1 2	Ru/C Ru/MCM-41	43 86	4.4 1.5	0.7 0.2	0.1 2.3	94.8 96.0	40.8 82.6	

^{*a*} Catalyst: 50 mg; solvent: water 50 g; benzyl alcohol: 1 g; H₂: 6 MPa; temperature: 323 K; propeller stir: 1000 rpm; reaction time: 20 h. ^{*b*} Ru/C metal loading: 5 wt%; Ru/MCM-41 metal loading: 3.7 wt%. ^{*c*} Yield of product 5 (cyclcohexanemethanol). The values are calculated by multiplying the conversion with the product selectivity.

to achieve a higher selectivity of cyclohexanemethanol. It can be seen that in entry 1 in Table 1, the selectivity of cyclohexanemethanol was 94.8% at 323 K, which was significantly higher than several reported values in the previous studies.^{2,3,10} This phenomenon may be explained by the less favored C-O bond cleavage, also known as hydrogenolysis, during mild temperature condition. Therefore, instead of mainly producing toluene and methylcyclohexane at high temperatures, the desired product cyclohexanemethanol could be obtained in high selectivity at mild temperatures. It was reported that lower reaction temperature and higher hydrogen pressure conditions were more suitable for hydrogenation instead of hydrogenolysis.¹¹ Accordingly, this work was mainly focused on the mild temperature and high pressure (323 K and 6 MPa H₂ pressure). Besides, the yield of cyclohexanemethanol was found to be greater when using Ru/ MCM-41 than using Ru/C in water solvent at 323 K (entry 2). For Ru/MCM-41, the hydrophilic property on the silica support surface may cause the catalyst to have a well-dispersion in water, which is exactly opposite to the Ru/C catalyst, since the charcoal surface is hydrophobic. This result has the same agreement with our previous study in hydrogenation of bisphenol A.¹² Therefore, the Ru/MCM-41 catalyst was chosen as the catalyst to examine the feasibility of other green solvents in the following sections.

The comparisons of different solvent systems and additives for the hydrogenation of benzyl alcohol using Ru/MCM-41 as the catalyst at 323 K are presented in Table 2. At first, the influence of using water as the solvent was examined and the results are shown in entries 1 and 2. The solubility of benzyl alcohol in water is about 4 g per 100 ml at 298 K, in other words, the saturation concentration of benzyl alcohol in water is about 0.37 M at room temperature. Therefore, the amount of benzyl alcohol used in the experiments was carefully selected not to exceed the saturation amount. It was found that the yield of cyclohexanemethanol was doubled while using water as the solvent compared to neat at the reaction time of 20 h. This confirms that the hydrophilic silica based catalyst is very suitable for catalyzing reactions in water.^{12,13} In addition, the results in entries 3 and 4 also indicated a radical change when using compressed CO₂/water as the solvent in hydrogenation of benzyl alcohol. The results may suggest some benefits of the compressed CO₂ existence. Several positive factors such as the increase of mass transfer and the decrease of viscosity of the reactants might influence the reaction rate of benzyl alcohol hydrogenation.^{6b} Later on, a neat benzyl alcohol with the



 Table 2
 Comparison of different solvent systems and additives used for the hydrogenation of benzyl alcohol^a

Entry	Solvent	Time (h)	Conv. (%)	Product selectivity (%)				
				2	3	4	5	$\mathrm{Yield}^{b}(\%)$
1 ^c	Neat	20	50	6.0	3.0	9.7	81.3	40.6
2	Water	20	86	1.5	0.2	2.3	96.0	82.6
3	Water	1.5	38	1.8	0.7	8.8	88.7	33.7
4	Water $+ CO_2$ (3 MPa)	1.5	53	2.7	0.8	8.4	88.1	46.7
5^d	Neat + $scCO_2$ (8 MPa)	5	25	3.4	0.9	12.9	82.8	20.7
6	Water + $CO_2(3 \text{ MPa})$	5	98	2.5	4.8	0.5	92.2	90.4
7^e	Water + acetic acid	5	93	5.8	16.4	1.0	76.8	71.4
8	Water	28	100	0	3.5	0	96.5	96.5

^{*a*} Catalyst: 3.7 wt% of Ru/MCM-41 50 mg; solvent: water 50 g; benzyl alcohol: 1 g; H₂: 6 MPa; temperature: 323 K; propeller stir: 1000 rpm. ^{*b*} Yield of product 5 (cyclcohexanemethanol). The values are calculated by multiplying the conversion with the product selectivity. ^{*c*} Magnetic stir bar: 1000 rpm. ^{*d*} CO₂-expanded benzyl alcohol (CXL system). ^{*e*} Acetic acid solution (0.01 M): 50 g.

addition of scCO₂ was also tested and the result is shown in entry 5. Under the condition of 8 MPa of scCO₂, benzyl alcohol was mostly expanded by CO₂ instead of dissolving in it due to the low solubility of benzyl alcohol in CO₂.¹⁴ Thus, the system became a CXL system and the yield was only 1/4 of that of the compressed CO₂/water system (entry 6). This result shows that CO₂ is a good additive for hydrogenation in water solvent system. The main reason may be attributed to the changing of acidity in the compressed CO₂/water system. According to the literature, water is categorized as a Class I liquid, which cannot be properly expanded by CO₂. Therefore, the properties of water can be remained, with the exception of acidity.^{6d} In this regard, carbonic acid (H₂CO₃) was formed when CO₂ was dissolved in water, and the measured pH value dropped instantly from 6.2 (DI water at 301 K) to 3.9 (CO₂-purged DI water at 301 K). The pH value of 3 MPa CO₂ compressed into water at 323 K was reported to be about 3.4, and no significant change was observed upon increasing the CO₂ pressure to over 3 MPa.¹⁵ Namely, the compressed CO₂/water system became a weak carbonic acid solution, which may directly increase the reaction rate of the aromatic hydrogenation of benzyl alcohol. To our interest, this phenomenon is one that deserves empirical scrutiny. Therefore, a simulated experiment of the carbonic acid-catalyzed effect was inspected by adding another additive, acetic acid, into the aqueous solution as the solvent. The pH value of 0.01 M acetic acid solution was measured as 3.4 at 323 K. The result of using acetic acid as the solvent is shown in entry 7. On comparison with compressed CO₂/water (entry 6), the yield of the fully hydrogenated product cyclohexanemethanol decreased. It was found that both the compressed CO2/water and the acetic acid had the ability to increase the reaction rate. From the literature, Takagi et al. had reported that adding lower relative permittivity (dielectric constant) of carboxylic acids (acetic acid, butyric acid, and lauric acid) into various organic solvents, the conversions of hydrogenation reactions were increased due to the decrease in relative permittivity of the mixture solutions.¹⁰ Unfortunately, the ratio of the hydrogenolysis products also rose in their study (increased by 20%). It is known that if an acid exists in the system, especially strong acid, the elimination reaction would be promoted due to the possible protonation of the hydroxyl group.¹⁶ However, in the present study, this phenomenon was restricted by the mild operating condition. Another possible

explanation for the enhancement of the reaction rate might lie in that the proton, H^+ , of acid or water could favor the cleavage of a metal–carbon bond.¹⁷ In this circumstance, once the cyclohexyl products were formed on the active sites of metal, the desorption rate may be enhanced in the presence of acid. Finally, the highest yield of cyclohexanemethanol (96.5%) was found at a reaction time of 28 h by using water as solvent (entry 8). This result suggested that water is a suitable solvent for the hydrogenation of benzyl alcohol to produce cyclohexanemethanol.

Hydrogenation of benzaldehyde

Another example from the benzyl chemical family, benzaldehyde, was also tested for the hydrogenation reaction. Some properties of benzaldehyde are quite similar to benzyl alcohol, including molecular weight, melting point and solubility in water. The entire hydrogenation of benzaldehyde can be considered as a series reaction. The carbonyl group (C=O) of benzaldehyde can be hydrogenated forming benzyl alcohol first, followed by further hydrogenation, the major product cyclohexanemethanol and the minor products toluene, methylcyclohexane and cyclohexenemethanol can also be formed eventually (Scheme 2). The results of hydrogenation of benzaldehyde are shown in Table 3. It was found that when using water as the solvent, selectivity of cyclohexanemethanol could be achieved at 86.4% in 30 h (entry 3). When using compressed CO₂/water, the yield of cyclohexanemethanol was increased nearly 6 times (entry 4 compare to entry 1) and 2 times (entry 5 compare to entry 2) at reaction times of 5 h and 10 h, respectively. Furthermore, entry 5 was observed with the highest yield of cyclohexanemethanol using only 1/3 of the reaction time than in water (entry 3). The improvement of using the compressed CO_2 /water



Scheme 2 Reaction pathway of benzaldehyde hydrogenation. 1: benzyl alcohol, 2: toluene, 3: methylcyclohexane, 4: cyclohexenemethanol, 5: cyclohexanemethanol.

Entry	Solvent			Product	Product selectivity (%)				
		Time (h)	Conv. (%)	1	2	3	4	5	$\mathrm{Yield}^{b}\left(\%\right)$
1	Water	5	99	91.5	0.5	0	0.8	7.2	7.1
2	Water	10	100	51.4	0.1	0	2.7	45.8	45.8
3	Water	30	100	5.8	0	4.9	2.9	86.4	86.4
4	Water $+ CO_2$ (3 MPa)	5	100	52.5	1.3	0.6	2.0	43.6	43.6
5	Water $+ CO_2$ (3 MPa)	10	100	5.9	1.1	3.8	0	89.2	89.2
6 ^{<i>c</i>}	Water + acetic acid	10	100	9.8	1.8	5.4	0.4	82.6	82.6

^{*a*} Catalyst: 3.7 wt% of Ru/MCM-41: 50 mg; solvent: water 50 g; benzaldehyde: 1 g; H_2 : 6 MPa; temperature: 323 K; propeller stir: 1000 rpm. ^{*b*} Yield of product 5 (cyclcohexanemethanol). The values are calculated by multiplying the conversion with the product selectivity. ^{*c*} Acetic acid solution (0.01 M): 50 g.



Scheme 3 Hydrogenation of benzoic acid.

system for hydrogenating benzaldehyde was not as extreme as for hydrogenating benzyl alcohol. This result may due to the fact that the hydrogenation of benzaldehyde is a series reaction. It is speculated that the acid had little or no effect on the first step of the process (Scheme 2), in which the carbonyl group (C==O) is reduced to a hydroxyl group (C=OH). In addition, entry 6 also shows the verification of acid-catalyzed effect in hydrogenation of benzaldehyde when using acetic acid solution as the solvent. The result was expected and confirmed to be nearly identical with the compressed $CO_2/water system$ (entry 5).

Hydrogenation of benzoic acid

In addition, a third compound, benzoic acid, was also chosen for the testing in this study. Although it is expected that benzoic acid should be difficult to convert into cyclohexanemethanol by gaseous hydrogen, the corresponding product cyclohexanecarboxylic acid, however, is still a valuable compound to synthesize for pharmaceutical application (Scheme 3). It is also noteworthy to point out an unexpected discovery from our experiment. Table 4 shows the results in the hydrogenation of benzoic acid. When using compressed CO₂/water as the solvent, the reaction rate of benzoic acid decreased. From the experimental results, it is reasonable to assume that the pK_a value of the reactants might also affect the reaction. Since the pH value of the saturated solution of benzoic acid is already about 3, the compressed CO₂ would not be able to alter the acidic condition. On the other hand, the pH value of the saturated solution of benzyl alcohol and benzaldehyde are both neutral. Therefore, the addition of the compressed CO2 could provide a weak acidic environment for the hydrogenation reaction to take place. In addition, it is speculated that protonation of the hydroxyl group could occur in the weak acidic environment (in our case, pH around 3).¹⁸ The protonated hydroxyl group could manipulate the electron density of the total compound causing a lowering of activation energy for the aromatic ring hydrogenation. Moreover, lowering the pH

 Table 4
 Hydrogenation of benzoic acid^a

Entry	Solvent	Time (h)	Conv. (%)
$ \frac{1}{2}{3^{b}} $	Water	2	100
	Water + CO ₂ (3 MPa)	2	70
	Water + acetic acid	2	100

^{*a*} Catalyst: 2.7 wt% of Ru/MCM-41, 25 mg; solvent: water, 100 g; benzoic acid: 0.25 g; H_2 : 6 MPa; temperature: 323 K; propeller stir: 1000 rpm. ^{*b*} Acetic acid solution (0.01 M): 50 g.

value of the system may promote the hydrogenolysis reaction since the elimination of the functional group could be catalyzed by acid. As a result, the reaction rate greatly enhanced and the selectivity for the hydrogenolysis products slightly increased. However, this is not the case for the hydrogenation of benzoic acid since the carboxylic protonation of benzoic acid can only be processed in strong acidic condition. Much to our surprise, the conversion of the benzoic acid hydrogenation somewhat followed a different trend, which actually decreased when adding CO₂ into the reaction system. A reasonable explanation could be provided here as that a dilution effect could occur when adding CO_2 into the reaction systems.¹⁹ When the compressed CO_2 was added into the gas phase, the mole fraction of hydrogen in the gas phase was decreased. This dilution effect of compressed CO₂ would reduce the gas-to-liquid mass transfer rate of hydrogen.^{19c} This phenomenon is relatively common when using $scCO_2$ for hydrogenation reactions and it may also occur in our experimental systems. According to the experimental data, the promotion effect should be more dominant than the dilution effect when adding CO₂ into the reaction system when hydrogenating benzyl alcohol and benzaldehyde and vice versa when hydrogenating benzoic acid. Furthermore, when using 0.01 M acetic acid solution as the solvent, no positive or negative influence was found since no promotion or dilution effect was expected in the system.

Advantages of CO₂ as the promoter

The comparison between CO_2 and an organic acid as a hydrogenation promoter is discussed below. Since CO_2 is gaseous under standard condition for temperature and pressure, the reaction products (excluding gaseous) and CO_2 could be easily separated by depressurization right after the reaction. The remaining liquid waste is therefore less contaminated and could be easily processed for disposal or recycling. However, when using an organic acid as a promoter, the residual acid could be a problem since the side product ester could be formed in the reaction with alcohol. On the other hand, when comparing CO_2 to inorganic acids (mineral acids), CO_2 is less toxic and environmental friendly, which could provide a greener operation. Therefore, using compressed CO_2 /water in the hydrogenation of benzyl alcohol and its derivatives could prevent these serious problems. In addition, the possible reverse water gas shift reaction which could produce a catalyst poison CO, should not be a critical issue in this study. The relatively mild reaction conditions and the biphasic environment of compressed CO_2 /water could help avoid catalyst poisoning.²⁰

Experimental

Catalyst preparation

Self-synthesized silica-supported Ru catalysts were prepared by chemical fluid deposition techniques and followed by the previously described experiments.^{12,21} The metal precursors including bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium [Ru(cod)(thmd)2, Strem] and ruthenium acetylacetonate [Ru(acac)₃, Strem] and the silica support MCM-41 (SiO₂, Sigma-Aldrich) were all used as received. In a typical trial, 285 mg of MCM-41 and ca. 87 mg of Ru(cod) (thmd)₂ were added together into a high pressure cell leading to a maximum metal ratio of 5% by weight. At 423 K, 10 MPa of H₂ and 10 MPa of CO₂ were premixed in a gas reservoir and injected into the cell for a reaction of 2 h. After the reaction, the cell was depressurized and flushed with CO2 for a few times to eliminate the unreacted metal precursors. The remaining powder sample was then collected for further analysis and catalytic testing. The metal loading of the catalysts were analyzed by energy dispersive X-ray spectroscopy (JEOL JSM-5600/Oxford 6587). The other catalyst properties and recycling procedures are provided in the supplementary information.

Hydrogenation of aromatic compounds

The experiments for the hydrogenation of benzyl alcohol and its derivatives were implemented in a semi-batch autoclave. Benzyl alcohol [99%, Sigma-Aldrich], benzaldehyde [99%, Alfa Aesar], benzoic acid [99%, Sigma-Aldrich], ruthenium on activated carbon [5% Ru/C, Sigma-Aldrich] and acetic acid [100%, Merck] were all used as received. In a typical trial, a mixture of 50 mg of the catalyst, 1 g of the benzyl alcohol and 50 g of deionized water were loaded into the high pressure autoclave. A CO₂ pressure of 3 MPa was first introduced into the cell and then followed by a H₂ pressure of 6 MPa. The reaction was set at a temperature of 323 K for a reaction time of 5 h. After the reaction, the system was cooled in an ice bath and the samples were extracted with diethyl ether. The products were then analyzed by a gas chromatography-mass spectrometry (GC-MS; HP5890II/ HP5972). A dimethylpolysiloxane based GC capillary column (Agilent HP-5MS) was used. The injector and the detector temperatures were set at 523 K and 533 K, respectively. A temperature program was employed for analysis starting at 323 K (hold for 5 min), followed by a 25 K min⁻¹ program rate to 473 K

(hold for 5 min). The products, toluene [HPLC-grade 99.9%, Echo], methylcyclohexane [HPLC-grade 99.9%, Echo], cyclohexanemethanol [99%, Sigma–Aldrich], cyclohexanecarboxylic acid [98%, Sigma–Aldrich] were used as the standard in the analysis.

Conclusions

In conclusion, five key points in the formation of cyclohexanemethanol by hydrogenation of benzyl alcohol and its derivatives were successfully demonstrated in this work. It can be summarized as the following: (i) the yield of cyclohexanemethanol when using the self-synthesized Ru/MCM-41 catalyst was found to be nearly 2 fold higher than that when using a commercial carbon supported catalyst in water; (ii) high conversion and product selectivity from the hydrogenation reactions of benzyl alcohol and benzaldehyde can be achieved in water at mild temperatures; (iii) after examining several green alternative solvents, a promotion effect was discovered when using the compressed carbon dioxide into water solvent system; (iv) water is a suitable solvent for the ring hydrogenation of aromatic compounds; (v) the compressed CO₂/water system could be very efficient for ring hydrogenation of aromatic alcohols and aldehydes. Last but not least, applying the idea of compressed CO₂/water for hydrogenation reactions can be considered as an inspiring example for green and sustainable chemistry.

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