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Title: Selective hydrogenation of benzonitrile in multiphase reaction systems including compressed carbon dioxide over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst

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1	Selective hydrogenation of benzonitrile in multiphase reaction systems including compressed
2	carbon dioxide over Ni/Al <sub>2</sub> O <sub>3</sub> catalyst
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14	
15	Abstract
16	
17	Selective hydrogenation of benzonitrile was studied with Ni/Al <sub>2</sub> O <sub>3</sub> in compressed CO <sub>2</sub> ,
18	hexane– $CO_2$ , ethanol– $CO_2$ and $H_2O$ – $CO_2$ systems. The phase behavior and the effect of $CO_2$ on
19	the conversion of benzonitrile and the yield of benzylamine were discussed. The reaction rate was
20	retarded in solventless, hexane and ethanol, but accelerated in water in the presence of compressed
21	CO <sub>2</sub> . The decrease in reaction rate was mainly ascribed to the formation of carbamate from
22	benzylamine and the intermediate 1-aminodibenzylamine reacting with CO <sub>2</sub> , and it precipitated

1 out to coat on the surface of catalyst in solventless and hexane, and the dilution effect of 2 compressed CO<sub>2</sub> in ethanol. But the yield of benzylamine was increased in solventless, hexane and 3 ethanol due to the following nucleophilic addition of benzylamine and benzylimine to 4 *N*-benzylidenebenzylamine was inhibited. Although, the reaction rate increased in water for the 5 enhanced solubility of H<sub>2</sub> and benzonitrile in H<sub>2</sub>O and decreased mass-transfer resistance in the 6 presence of compressed CO2, the yield of benzylamine decreased because of the acidic nature of 7 H<sub>2</sub>O-CO<sub>2</sub> favorites the elimination of NH<sub>3</sub> and the formation of NH<sub>4</sub>HCO<sub>3</sub>. Accordingly, the possible reaction pathway of benzonitrile hydrogenation was proposed for all the studied systems. 8 9

10 Keywords: benzonitrile, hydrogenation, nickel, compressed carbon dioxide, multiphase reaction



#### 1 1. Introduction

2

3 Aromatic primary amines are important chemical compounds commonly used as 4 intermediates for the pharmaceutical, agrochemical and textile industries. The heterogeneous 5 catalytic hydrogenation of aromatic nitriles is an important process to produce aromatic primary 6 amines. However, during the hydrogenation of aromatic nitriles, several byproducts such as 7 secondary amine and enamine are usually formed, resulting in a loss of yield toward aromatic 8 primary amines [1, 2]. For the selective hydrogenation of nitriles to primary amines, the rate and the product composition are primarily depending on the type of catalyst. Raney Ni, Raney Co, 9 10 supported Ni, Pd, Pt, Ru, and Rh are suitable catalysts [2]. Supported Ni catalysts are often used 11 because of their low cost [3], and moderate activity and selectivity to primary amines [4-7]. In the 12 gas phase hydrogenation of benzonitrile with 5% Ni on various supports, it was reported that the 13 activity of the catalysts was in an order of  $Al_2O_3 > TiO_2 > SiO_2 - Al_2O_3 > SiO_2$  [8]. In addition, the type 14 of solvent, reactant concentration, reaction conditions and additives (e.g. ammonia) also play 15 important roles [1, 2].

The multiphase system containing compressed  $CO_2$  has been paid much attention recently [9-12]. The pressurization of liquid reaction mixtures with  $CO_2$  will be effective for accelerating the rate of reaction, modifying the product selectivity, and making it easy to separate and recycle the catalyst. Different types of multiphase systems containing compressed  $CO_2$  could be designed and applied for various chemical transformations [10]. For example, Eckert et al. investigated  $CO_2$ -expanded ethanol for the heterogeneous hydrogenation of benzonitrile and phenylacetonitrile with NiCl<sub>2</sub>/NaBH<sub>4</sub>. The yield of primary amines increased to 98% because the primary amines

1	were protected by $CO_2$ and their further hydrogenation to the secondary amines were effectively
2	suppressed. They also studied CO <sub>2</sub> -expanded tetrahydrofuran for homogeneous hydrogenation of
3	the same nitriles with RhH(P-i-Ph <sub>3</sub> ) <sub>3</sub> , in which, the primary amines are separated in situ in the
4	form of solid carbamic acid and/or ammonium carbamates while the catalysts remain in the
5	solution [13]. The hydrogenation of nitrile was performed in supercritical CO <sub>2</sub> over Pd/MCM-41
6	and Ni/MCM-41, respectively. With Pd/MCM-41, the selectivity to benzylamine was 91% at 90%
7	conversion. It is possible to tune the selectivity from primary amine to secondary amine by
8	varying the CO <sub>2</sub> pressure. With Ni/MCM-41, dibenzylamine was produced as the main byproduct
9	with a poor selectivity to benzylamine of 37.5% [14]. The use of large amount of noble metal
10	catalyst makes the chemical process too expensive to apply in the large scale industrial utilization.
11	Therefore, development of efficient non-noble metal catalysts like Ni-based catalyst and green
12	catalytic reaction system is a big challenge to the researchers.
13	In this work, the hydrogenation of benzonitrile was studied with Ni/Al <sub>2</sub> O <sub>3</sub> in compressed CO <sub>2</sub> ,
14	hexane– $CO_2$ , ethanol– $CO_2$ and $H_2O$ – $CO_2$ systems. For comparison, the reaction was also
15	examined in solventless system, hexane, ethanol and water. The phase behavior and the functional
16	roles of CO <sub>2</sub> were discussed, and the possible reaction pathway was proposed in multiphase
17	systems containing compressed CO <sub>2</sub> .

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### 19 2. Experimental

20 2.1. Chemicals, catalyst preparation and characterization

21

22 Benzonitrile, hexane, ethanol, benzaldehyde, benzyl alcohol, benzylamine, dibenzylamine,

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tribenzylamine, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub> are of analytical grade and used without further purification. Deionized water and gases of H<sub>2</sub> (99.999%), N<sub>2</sub> (99.999%), CO<sub>2</sub> (99.999%) and NH<sub>3</sub> (99.999%) were used as delivered. *N*-benzylidenebenzylamine was prepared by condensing of benzaldehyde and benzylamine in ethanol at room temperature for 24 h, and obtained through rotary evaporation, and analyzed with a gas chromatograph and gas chromatography/mass spectrometry.

Alumina-supported Ni catalyst was prepared by co-precipitation using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 7 Al(NO<sub>3</sub>)<sub>3</sub> with a Ni/Al atomic ratio of 1/1. After dried at 120 °C for 12 h, the sample was calcined 8 9 at 450 °C for 5 h under air in Muffle oven. Before each hydrogenation run, a certain amount of 10 samples was reduced under H<sub>2</sub> flow at 580 °C for 2 h. The Ni loading in the calcined samples of 11 Ni/Al<sub>2</sub>O<sub>3</sub> was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, 12 iCAP6300, Thermo USA). The structural properties of catalysts were examined by X-ray diffraction (XRD, Philips PW1710 BASED) and transmission electron microscopy (TEM, 13 14 JEM-2000EX). Temperature-programmed reduction (TPR) was carried out by heating 50 mg catalyst sample under  $H_2/N_2$  at 10 °C ·min<sup>-1</sup> up to 800 °C. 15

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#### 17 2.2. Hydrogenation of benzonitrile

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The hydrogenation of benzonitrile was carried out at 80  $^{\circ}$ C in a 50 ml autoclave. The reactor was charged with 2 ml benzonitrile (19.6 mmol) and a catalyst sample, flushed with N<sub>2</sub>, and heated with a water bath. After introduction of 4 MPa H<sub>2</sub>, liquid CO<sub>2</sub> was flowed into the reactor with a high-pressure liquid pump (Jasco SCF-Get) to the desired pressure when necessary. The

1	reaction was conducted with a continuously stirring stirred with a magnetic stirrer. The reaction
2	was carried out with a stirring speed of 1200 rpm, at which the mass transport limitation was
3	confirmed to remove completely for that the reaction rate did not change after the stirring speed
4	was increased up to 800 rpm. After reaction, the reactor was cooled with an ice-water bath,
5	depressurized carefully. Then the reaction mixture was dissolved with about 30 ml ethanol and the
6	liquid products were centrifuged and analyzed with a gas chromatograph (GC-Shimadzu-2010,
7	FID, Capillary column, Rtx-5 30 m $\times$ 0.25 mm $\times$ 0.25 $\mu m$ ), and identified by gas
8	chromatography/mass spectrometry (GC/MS, Agilent 5890). The extent of error for the
9	conversion and yield was in a range of $\pm 2\%$ . The carbon balance was calculated based on reactant
10	and all the detected products such as benzylamine, N-benzylidenebenzylamine, dibenzylamine,
11	tribenzylamine, benzaldehyde and benzylalcohol with external standard method, the data was near
12	to 99.8%. The reaction proceeds without adding any solvent except for the reactants, naming
13	"solventless system". Hydrogenation reactions in ethanol, hexane, water, ethanol-CO <sub>2</sub> ,
14	hexane-CO2 and H2O-CO2 were conducted with the similar procedures. For some cases, the
15	carbamic acid and/or ammonium carbamates were formed and precipitated as white solid such as
16	in dense phase CO <sub>2</sub> and hexane-CO <sub>2</sub> . The reaction results are reproducible at same reaction
17	conditions.

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### 19 2.3. Visual observation of the phase behavior

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The observation of the phase state was carried out in an 85 ml high-pressure view cell. The observations were made with a similar volumetric ratio of benzonitrile to the reactor volume as

used in the hydrogenation runs. In the typical process, benzonitrile (3.4 ml) was added and the reactor was heated up to 80 °C, H<sub>2</sub> (4 MPa) and then liquid CO<sub>2</sub> was introduced into the reactor to the required pressure. At each pressure the mixture was stirred for several minutes, and then the stirring was stopped and the phase behavior was observed by the naked eye through the transparent sapphire windows.

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Fig. 1. Lift: XRD patterns of the Ni/Al<sub>2</sub>O<sub>3</sub> samples (a) precursor dried at 120 °C, (b) calcined at
450 °C for 5 h under air, (c) reduced at 580 °C with H<sub>2</sub> for 2 h, (∇) NiAl(CO<sub>3</sub>)(OH)<sub>3</sub>, (□) NiO,
(○) Ni, and TPR of calcined Ni/Al<sub>2</sub>O<sub>3</sub> samples (inset). Right: TEM of reduced Ni/Al<sub>2</sub>O<sub>3</sub> sample.

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### 12 3. Results and discussion

- 13 3.1. Catalyst characterization
- 14

The XRD patterns of Ni/Al<sub>2</sub>O<sub>3</sub> are presented in Fig. 1. The co-precipitated intermediate exhibited the characteristic diffraction peaks of nickel aluminum carbonate hydroxide, i.e., NiAl(CO<sub>3</sub>)(OH)<sub>3</sub> (PDF No. 48-0593), but its crystalline was somewhat poor (Fig. 1a). After calcination, the sample showed a broad NiO diffraction, but no Al<sub>2</sub>O<sub>3</sub> and NiAl<sub>2</sub>O<sub>4</sub> spinel were

identified, indicating that Al species were likely to be well mixed in the bulk of NiO (Fig. 1b) [15]. 1 2 In addition, only one main reduction peak centered at 555 °C was found from the TPR profile of 3 calcined Ni/Al<sub>2</sub>O<sub>3</sub> sample, indicating the NiO species was homogeneously dispersed (Fig. 1 inset). 4 For the sample reduction at 580 °C for 2 h, it showed sharp peaks of Ni diffraction and the average particle size of Ni was ca. 7.3 nm as determined from the Ni (111) facet by equation (Fig. 1c). The 5 6 peaks of NiO diffraction disappear, indicating the most NiO was reduced to the metallic Ni. Based 7 on the TPR, the amount of hydrogen consumption of the reduction peaks at 360-790 °C was 0.332 8 mmol as estimated by using nano CuO as reference, it was nearly to the amount required for full 9 reduction of NiO on Ni/Al<sub>2</sub>O<sub>3</sub>, which was also confirmed by the XRD analysis. TEM image 10 indicated the average particle size of Ni particles was 6.9 nm (Fig. 1d), which is accordant with the XRD results. The loading of Ni was 41.4% as measured by ICP-OES, which is close to the 11

12 theoretical value of 46.7%.



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14 Scheme 1. Proposed reaction pathways of benzonitrile hydrogenation in CO<sub>2</sub>, hexane–CO<sub>2</sub> and

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17 3.2. Hydrogenation of benzonitrile in different media

<sup>15</sup> ethanol– $CO_2$ .

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As described in scheme 1, generally, benzonitrile is hydrogenated to benzylimine 2, and it is then hydrogenated to benzylamine 3 and condensed with benzylamine 3 to 1-amino dibenzylamine 5; 1-amino dibenzylamine 5 can be transformed to benzylamine 3 as well as deaminated to *N*-benzylidenebenzylamine 6 and then hydrogenated to dibenzylamine 7. In the presence of CO<sub>2</sub>, benzylamine 3 is transformed to carbamate 4, carbamate 4 cannot act as a nucleophile to react with benzylimine 2, so the nucleophilic addition between benzylamine 3 and benzylimine 2 is inhibited [13, 14].

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Fig. 2. Hydrogenation of benzonitrile in (a) solventless systems, (b) 10 MPa CO<sub>2</sub>. Reaction
conditions: 2 ml benzonitrile, 0.1 g Ni/Al<sub>2</sub>O<sub>3</sub>, 4 MPa H<sub>2</sub>, 80 °C, (■) conversion of benzonitrile,

13 yield of  $(\triangle)$  *N*-benzylidenebenzylamine,  $(\bigcirc)$  benzylamine,  $(\diamondsuit)$  dibenzylamine.

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15 *3.2.1. Hydrogenation of benzonitrile in compressed CO*<sub>2</sub>, *hexane–CO*<sub>2</sub>, *ethanol–CO*<sub>2</sub>

16

17 Fig. 2 shows the evolution of product distribution along with the process of benzonitrile

18 hydrogenation over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the absence and presence of compressed CO<sub>2</sub>. The rate of

benzonitrile conversion in the absence of CO2 was faster than that in 10 MPa CO2, complete 1 2 conversion presented at 10 h for the former, but it presented at 15 h for the latter case. And in both 3 the systems, N-benzylidenebenzylamine was produced as the predominant intermediate product at 4 the beginning of reaction. In the absence of CO<sub>2</sub>, N-benzylidenebenzylamine was converted to 5 both benzylamine and dibenzylamine with the extension of reaction and the yield of benzylamine 6 dibenzylamine reached 74.6% 23.7% conversion of and and at complete 2a). In 10 MPa CO<sub>2</sub>, 7 N-benzylidenebenzylamine after reaction for 25 h (Fig. 8 *N*-benzylidenebenzylamine was converted to benzylamine with the extension of reaction, and the 9 yield of benzylamine reached 96.5% at the end of reaction, but dibenzylamine did not change 10 anymore and its yield was only 2.8% (Fig. 2b). Therefore, the product distribution changed largely 11 and the benzylamine was yielded much more in the presence of CO<sub>2</sub>, and it is about 20% higher 12 than that in the solventless conditions.

Table 1 shows the results of the hydrogenation of benzonitrile in hexane and hexane-10 MPa 13 CO2. The rate of benzonitrile conversion in hexane was faster than that in hexane-10 MPa (entries 14 15 1, 5). N-benzylidenebenzylamine was also produced as the predominant intermediate product at 16 the beginning of the reaction in these both systems. In hexane, when both benzonitrile and 17 N-benzylidenebenzylamine were completely transformed after 24 h, the yield of benzylamine and 18 dibenzylamine was 72.8% and 26.6%, respectively (entry 4). When 10 MPa CO<sub>2</sub> was introduced 19 into hexane, the yield of benzylamine increased to 94.4%, and the yield of dibenzylamine was 20 5.5%, it increased slightly during the reaction process (entries 5-8). It suggested also that the 21 presence of compressed CO<sub>2</sub> could prohibit the formation of dibenzylamine.

22 Fig. 3 shows the evolution of products in ethanol and ethanol-10 MPa CO<sub>2</sub>. The

1 hydrogenation rate of benzonitrile in ethanol was faster than that in ethanol-CO<sub>2</sub>. 2 N-benzylidenebenzylamine was also produced as the predominant intermediate product at the beginning of reaction. In ethanol, when both of the hydrogenation of benzonitrile and 3 4 *N*-benzylidenebenzylamine were completed, the yield of benzylamine and dibenzylamine was reached to 82.3% and 16.3%, respectively (Fig. 3a). However, when 10 MPa CO<sub>2</sub> was introduced 5 into ethanol, the yield of benzylamine increased to 95.6%, and the yield of dibenzylamine was 6 7 2.3% and changed lightly during the reaction process (Fig. 3b). It is similar to the cases above discussed for the solventless and hexane, that the presence of compressed CO<sub>2</sub> retarded the rate of 8 9 benzonitrile conversion, inhibited the formation of dibenzylamine and enhanced the yield of 10 benzylamine.

11

En tre -	Calcoret		Conv.	onv. Yield (%)			
Entry	Solvent	t (n)	(%)	BBA	BA	DBA	- Kate (n)
1	5 ml hexane	3	100	46.4	43.9	9.7	59.4 (26.1)
2		12	100	15.0	66.1	18.9	- (9.8)
3		15	100	11.2	74.0	14.8	- (8.8)
4		24	100	0.6	72.8	26.6	- (5.4)
5	5 ml hexane +	6	72.0	42.0	26.1	3.9	21.4 (7.8)
6	10 MPa CO <sub>2</sub>	16	100	26.1	69.8	4.1	- (7.8)
7		24	100	7.9	86.6	5.5	- (6.4)
8		30	100	0.1	94.4	5.5	- (5.6)

#### 12 **Table 1** Hydrogenation of benzonitrile in hexane and hexane–CO<sub>2</sub>

11

Reaction conditions: 2 ml benzonitrile, 0.1 g Ni/Al<sub>2</sub>O<sub>3</sub>, 80 °C, 4 MPa H<sub>2</sub>. BBA: *N*-benzylidenebenzylamine, BA: benzylamine, DBA: dibenzylamine.
<sup>a</sup> the reaction rate of benzonitrile hydrogenation, which was given as the overall rate of
benzylamine conversion normalized by the number of active sites over the specified time; values
in parentheses indicate rate of the hydrogenation of benzonitrile into benzylamine. The number of
active sites was calculated using the average Ni diameters (*d*) via the following equation:
Dispersion = 6(v<sub>m</sub>/a<sub>m</sub>)/d, where v<sub>m</sub> and a<sub>m</sub> are equal to 10.95 Å<sup>3</sup> and 6.51 Å<sup>2</sup> respectively, for Ni.



9 **Fig. 3.** Hydrogenation of benzonitrile in (a) 5 ml ethanol, (b) 5 ml ethanol–10 MPa CO<sub>2</sub>. Reaction

10 conditions: 2 ml benzonitrile, 0.1 g Ni/Al<sub>2</sub>O<sub>3</sub>, 4 MPa H<sub>2</sub>, 80 °C, (■) conversion of benzonitrile,

11 yield of  $(\triangle)$  *N*-benzylidenebenzylamine, (O) benzylamine,  $(\diamondsuit)$  dibenzylamine.

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Water is the most abundant, cheap, safe, and environmentally benign solvent in nature and the study of organic reaction in/on water is an important theme of current research from the point of green chemistry [16-18]. The pressurization of H<sub>2</sub>O with CO<sub>2</sub> could make it become more effective in separating and recycling of catalyst, accelerating the rate of reaction, and modifying

1	the product selectivity [19-23]. Herein, the combination of $H_2O$ and $CO_2$ was first used for the
2	hydrogenation of benzonitrile to study the effect of H <sub>2</sub> O and CO <sub>2</sub> in this reaction, and the results
3	are listed in Table 2. The conversion of benzonitrile in $H_2O-10$ MPa $CO_2$ (97.0%) was higher than
4	that in $H_2O$ (82.0%) (entries 1, 5). N-benzylidenebenzylamine was also produced as the
5	predominant intermediate product at the beginning of reaction, and then it was transformed to
6	benzylamine and dibenzylamine. The yield of benzylamine in $H_2O-10$ MPa $CO_2$ (51.2%) was
7	lower than that in $H_2O$ (62.1%) but the yield of dibenzylamine in former (37.0%) was little higher
8	than that in $H_2O$ (34.9%) under the complete conversion of benzonitrile and
9	<i>N</i> -benzylidenebenzylamine (entries 4, 8). In addition, tribenzylamine was produced in H <sub>2</sub> O–CO <sub>2</sub>
10	but not in H <sub>2</sub> O. The results obtained herein were totally different from the above three systems,
11	that the presence of compressed $CO_2$ could accelerate the reaction rate and benefit the formation
12	of dibenzylamine and tribenzylamine in water; it is contradiction to the results obtained in both
13	hexane and ethanol. This will be discussed from the phase behavior and the reaction pathway later.
14	

Enter	Solvent	t	Conv.			Yield	(%)			$\mathbf{D}_{\mathbf{r}}$
Enuy		(h)	(%)	BBA	BA	DBA	TBA	BAE	BAL	Kate (n)
1	5 ml	1	82.0	79.6	_	0.1	_	2.3	_	146.0 (-)
2	H <sub>2</sub> O	2	100	39.2	40.8	19.2	_	0.1	0.7	- (36.3)
3		3	100	19.7	53.8	23.8	_	_	2.7	- (31.9)
4		12	100	0.8	62.1	34.9	_	_	2.2	- (9.2)
5		1	97.0	51.7	7.8	22.8	4.5	9.6	0.6	172.7 (13.9)

15 <b>Table 2</b> Hydrogenation of benzonitrile in H <sub>2</sub> O and H <sub>2</sub> O–C	O <sub>2</sub>
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	6	5 ml	2.5	100	43.8	14.5	30.9	9.8	0.5	0.4	-(10.3)	
	7	$H_2O +$	5	100	13.8	42.4	33.7	9.6	_	0.5	-(15.1)	
	8	10 MPa CO <sub>2</sub>	6.5	100	0.9	51.2	37.0	9.8	_	1.1	- (14.0)	
1	Reactio	on conditi	ons: 2	ml be	nzonitrile	e, 0.1	g Ni/Al	l <sub>2</sub> O <sub>3</sub> , 80	°C,	4 MPa	H <sub>2</sub> . BBA:	
2	N-benzylidenebenzylamine, BA: benzylamine, DBA: dibenzylamine, TBA: tribenzylamine, BAE:											
3	Benzaldehyde, BAL: Benzyl alcohol.											
4												
5	3.3. Di	scussion										
6												
7	Tl	ne presenc	e of co	ompresse	d CO <sub>2</sub>	could re	tard the	rate of	benzo	onitrile co	nversion in	
8	solvent	less, hexar	e and et	hanol, bi	ut acceler	rate the r	ate in wa	ater. This	could	be explain	ned from the	
9	phase l	behavior. F	ig. 4 sho	ows the p	hotograp	ohs of the	e states o	f reactar	ıt mixtu	ire during	the reaction	
10	in diffe	erent reaction	on syster	ms. In so	lventless	system,	the liqui	id benzoi	nitrile s	lightly ex	panded with	
11	the intr	oduction o	f CO <sub>2</sub> ar	nd the ma	aximum v	volume v	vas obtai	ned at 11	MPa (	$CO_2$ , and a	a solid phase	
12	present	ted with the	e introdu	ction of	CO <sub>2</sub> (Fig	. 4a and	Fig. S1,	S2). In h	exane,	the liquid	benzonitrile	
13	and he	xane gradu	ually ex	panded v	with the	introduc	tion of	$CO_2$ and	the m	aximum	volume was	
14	obtaine	ed at 11~12	MPa Co	$O_2$ , then $I$	liquid mi	xture vol	ume dec	reased a	nd final	ly formed	a single gas	
15	phase at 13.4 MPa CO <sub>2</sub> . The product benzylamine completely transformed from liquid to solid in											
16	the pre	sence of C	$O_2$ and p	precipitat	ed out fro	om solut	ion, even	though	the solution	ution trans	sformed into	
17	a singl	e gas phas	e at 11	MPa (Fi	g. 4b and	d Fig. Sa	3, S4). Iı	n ethano	l, the li	iquid benz	zonitrile and	
18	ethanol gradually expanded with the introduction of CO <sub>2</sub> and transformed into a single gas phase											

1	at 15.6 MPa CO <sub>2</sub> . The product benzylamine and ethanol gradually expanded with the introduction
2	of CO <sub>2</sub> also and the maximum volume was obtained at 8~11 MPa CO <sub>2</sub> , then liquid mixture
3	volume decreased from 12 to 18 MPa CO <sub>2</sub> . However, the product benzylamine transformed from
4	liquid to solid and precipitated out from ethanol when the reactor cooled from 80 °C to room
5	temperature, depressurizing of CO2. (Fig. 4c and Fig. S5, S6). In water, benzonitrile was
6	immiscible with water, the liquid benzonitrile and water expanded with the introduction of $\mathrm{CO}_2$
7	and the maximum volume was obtained at 10~14 MPa CO <sub>2</sub> (Fig. 4d and Fig. S7). The formed
8	benzylamine can be miscible with water, the volume of the liquid mixture of benzylamine and
9	water changed slightly with the introduction of CO <sub>2</sub> , and benzylamine transformed from liquid to
10	solid when the reactor cooled from 80 $^{\circ}$ C to room temperature, depressurizing of CO <sub>2</sub> (Fig. S8).
11	However, dibenzylamine and tribenzylamine were immiscible with water. When CO <sub>2</sub> was
12	introduced into dibenzylamine, the phase behavior didn't change, even the temperature was cooled
13	to room temperature and waiting for 24 h, but the viscosity of dibenzylamine increased obviously
14	which indicated the formation of dibenzylamine carbamate (photographs were not show). So when
15	the product benzylamine, dibenzylamine and tribenzylamine were mixed with water, two liquid
16	phases were formed, and the phase behavior didn't change with the introduction of CO <sub>2</sub> , but the
17	product benzylamine transformed from liquid to solid when the reactor cooled from 80 °C to room
18	temperature, depressurizing of $CO_2$ and waiting for 2 h (Fig. S9). With the introduction of 10 MPa
19	CO <sub>2</sub> , the liquid phase of benzonitrile in solventless system, hexane, ethanol and water were
20	expanded; the product benzylamine was transformed to carbamate and precipitated out in CO <sub>2</sub> and
21	hexane– $CO_2$ but dissolved in ethanol– $CO_2$ and $H_2O$ – $CO_2$ under the reaction conditions, but they
22	precipitated out in ethanol–CO <sub>2</sub> and H <sub>2</sub> O–CO <sub>2</sub> also after cooling and depressurizing.

1 In this work, the presence of compressed  $CO_2$  may affect the reaction rate from (1) increasing 2 the solubility of H<sub>2</sub> in the liquid phase (positive); (2) forming carbamate and/or coating on the 3 surface of catalyst (negative); (3) the dilution effect (negative). With the introduction of CO<sub>2</sub>, the 4 positive effect of the increasing of H<sub>2</sub> solubility was more significant than the negative one of 5 dilution effect, but they might be counteracted each other in some cases, and so the reaction rate of 6 benzonitrile to benzylamine decreased due to the negative effect of the precipitation of carbamate 7 in solventless and hexane. However, in ethanol and water, the formed carbamate is soluble in the solution. When 10 MPa CO<sub>2</sub> was introduced into ethanol (entries 3 in Table S1), the solution was 8 9 largely expanded for large amount of CO<sub>2</sub> dissolved in it, therefore the reaction rate decreased due 10 to the significant dilution effect of CO2. However, H2O could not be expanded due to low 11 solubility of CO<sub>2</sub> in it, and so the reaction rate in water was increased with introduction of CO<sub>2</sub>, 12 which is benefited from the enhanced concentration of gaseous reactant H<sub>2</sub>.







g. 4. These obliavior of the reaction inixture before and after reaction at so C in (a) solventiess
system (conditions for after reaction: 2.42 ml benzylamine, 1.06 ml dibenzylamine and 1.6 MPa
H<sub>2</sub>) and 10 MPa CO<sub>2</sub> (conditions for after reaction: 3.64 ml benzylamine and 1.6 MPa H<sub>2</sub>), (b) 8.5
ml hexane (conditions for after reaction: 2.42 ml benzylamine, 1.06 ml dibenzylamine and 1.4
MPa H<sub>2</sub>) and 8.5 ml hexane–10 MPa CO<sub>2</sub> (conditions for after reaction: 3.64 ml benzylamine and
1.4 MPa H<sub>2</sub>), (c) 8.5 ml ethanol (conditions for after reaction: 2.42 ml benzylamine, 1.06 ml
dibenzylamine and 1.4 MPa H<sub>2</sub>) and 8.5 ml ethanol–10 MPa CO<sub>2</sub>(conditions for after reaction:

1	3.64 ml benzylamine and 1.4 MPa H <sub>2</sub> ), (d) 8.5 ml H <sub>2</sub> O (conditions for after reaction: 1.71 m
2	benzylamine, 1.69 ml dibenzylamine and 1.4 MPa H <sub>2</sub> ) and 8.5 ml H <sub>2</sub> O-10 MPa CO <sub>2</sub> (conditions
3	for after reaction: 1.2 ml benzylamine, 1.53 ml dibenzylamine, 0.62 ml tribenzylamine and 1.4
4	MPa H <sub>2</sub> ). Conditions for before reaction: 3.4 ml benzonitrile and 4 MPa H <sub>2</sub> for all the systems.

5

N-benzylidenebenzylamine was produced as the predominant product at the beginning of 6 7 reaction in all the studied systems, then it transformed to benzylamine or/and dibenzylamine. It has been reported that N-ethylethylimine (CH<sub>3</sub>CH=NCH<sub>2</sub>CH<sub>3</sub>) was produced as intermediate for 8 9 the hydrogenation of acetonitrile over the supported nickel catalysts [4, 6]. The yield of 10 benzylamine increased remarkable with the introduction of CO2 into solventless, hexane and 11 ethanol. With comparing to solventless system and ethanol, the yields of benzylamine were higher, 12 but the yields of N-benzylidenebenzylamine 6 were lower in 10 MPa CO<sub>2</sub> and in ethanol-CO<sub>2</sub> at 13 similar conversions (Fig. 2, 3). According to scheme 1, once benzylamine was produced, a part of it was transformed to carbamate 4 by reacting with CO<sub>2</sub> [13, 14], carbamate 4 cannot act as a 14 15 nucleophile to interact with benzylimine 2 [13], so the formation of intermediate 16 N-benzylidenebenzylamine 6 was inhibited with the introduction of CO<sub>2</sub>. However, a major part of 17 benzylamine was condensed with benzylimine 2 to 1-amino dibenzylamine 5 on the surface of 18 catalyst. In the absence of CO<sub>2</sub>, 1-amino dibenzylamine 5 was transformed to benzylamine 3 as 19 well as to N-benzylidenebenzylamine 6 and then hydrogenated to dibenzylamine 7. In the 20 presence of CO<sub>2</sub>, 1-amino dibenzylamine 5 could also be converted to carbamate 8, so the further 21 deamination of 1-amino dibenzylamine 5 to N-benzylidenebenzylamine 6 and then hydrogenation 22 to dibenzylamine 7 was inhibited, resulting in high yield of benzylamine in 10 MPa CO<sub>2</sub>,

hexane-CO2 and ethanol-CO2. These results could be further confirmed by the reaction of 1 2 *N*-benzylidenebenzylamine **6** as starting reactant (Table 3). In the presence of 4 MPa  $H_2$  and 4 3 MPa NH<sub>3</sub>, the conversion increased from 35.9% to 72.8% and the selectivity to benzylamine 4 increased from 87.0% to 94.9% when 10 MPa CO<sub>2</sub> was introduced into hexane (entries 1, 2), and the conversion increased from 91.3% to 94.8% and the selectivity to benzylamine increased from 5 6 61.6% to 97.1% when 10 MPa CO<sub>2</sub> was introduced into ethanol (entries 3, 4). In the presence of much excess NH<sub>3</sub>, N-benzylidenebenzylamine 6 was mainly transformed to 1-amino 7 dibenzylamine 5, it can be hydrogenated to benzylamine 3 and dibenzylamine 7, and converted to 8 9 carbamate 8 in the presence of  $CO_2$ . The formation of carbamate 8 inhibited the deamination of 10 1-amino dibenzylamine 5 and the further hydrogenation to dibenzylamine 7, and the desired product benzylamine can also be converted to carbamate 4. So the yield of benzylamine was high 11 12 in the presence of CO<sub>2</sub>.

13

Entry	Salvant	CO <sub>2</sub> (MPa)	$C_{ODV}(9/)$ –	Sel. (%)		
Епцу	Solvent		Conv. (76) –	BA	DBA	
1	hexane	_	35.9	87.0	13.0	
2	hexane	10	72.8	94.9	5.1	
3	ethanol	_	91.3	61.6	38.4	
4	ethanol	10	94.8	97.1	2.9	

### 14 **Table 3** Hydrogenation of *N*-benzylidenebenzylamine

15 Reaction conditions: 1.92 g BBA, 0.1 g Ni/Al<sub>2</sub>O<sub>3</sub>, 5 ml solvent, 4 MPa H<sub>2</sub>, 4 MPa NH<sub>3</sub>, 80 °C, 16

16 h for hexane and 5 h for ethanol. BBA: N-benzylidenebenzylamine, BA: benzylamine, DBA:

1 dibenzylamine.

2

3 The benzylimine 2 has not been confirmed by direct observation, which is attributed to its 4 high reactivity [24]. Although 1-amino dibenzylamine 5 has never been observed, it is assumed to 5 be the intermediate according to literature [24, 25]. Carbamate 4 may decompose to benzylamine, 6 and carbamate 8 and intermediate 5 may decompose to N-benzylidenebenzylamine 6, and 7 carbamate 9 to dibenzylamine 7 when it dissolve in ethanol or/and during the GC analysis. The yield of benzylamine decreased with the introduction of CO<sub>2</sub> into water. It is 8 9 contradiction to the results obtained in solventless, hexane and ethanol. The yield of 10 dibenzylamine in H<sub>2</sub>O-10 MPa CO<sub>2</sub> was higher than that in H<sub>2</sub>O, and tribenzylamine was 11 produced in H<sub>2</sub>O-CO<sub>2</sub> but not in H<sub>2</sub>O. The reaction pathways of benzonitrile hydrogenation in 12 H<sub>2</sub>O-CO<sub>2</sub> are proposed in scheme 2. Benzylamine 3, 1-amino-dibenzylamine 5 and 13 dibenzylamine 7 are produced and could be converted to corresponding carbamate by reacting with  $CO_2$  also. Benzaldehyde is formed from the hydrolysis of benzylimine 2 followed by the 14 15 elimination of NH<sub>3</sub> [1]. 1-amino-dibenzylamine 5 deaminated to N-benzylidenebenzylamine 6 and 16 then hydrogenated to dibenzylamine 7. Benzylimine 2 condensed with dibenzylamine 7 to 17 gem-diamine 14, which hydrogenated and deaminated to tribenzylamine. In  $H_2O-CO_2$  system, the 18 acidity of the solution increases in pH value by about 3 at a wide range of pressures and 19 temperatures [26, 27]. Herein, the acidic nature of H<sub>2</sub>O-CO<sub>2</sub> (pH≈2.9) could accelerate the 20 elimination of NH<sub>3</sub> and form NH<sub>4</sub>HCO<sub>3</sub>, so the amount of benzaldehyde, dibenzylamine and 21 tribenzylamine in H<sub>2</sub>O–CO<sub>2</sub> is higher than that in H<sub>2</sub>O. In addition, tribenzylamine may be formed 22 from the condensation of dibenzylamine and benzaldehyde to carbinolamine 13 followed by the

direct hydrogenolysis. The carbinolamine **13** and *gem*-diamine **14** cannot undergo  $H_2O$  and  $NH_3$ elimination to an imine, because no hydrogen atom is available on the central N atom, so the direct hydrogenolysis is considered to be responsible for the formation of a tertiary amine in this reaction [2]. Benzaldehyde could be hydrogenated to benzyl alcohol and condensed with benzylamine to *N*-benzylidenebenzylamine **6**. Benzylamine cannot be transformed to dibenzylamine in  $H_2O-CO_2$  when benzylamine was used as reactant under the similar conditions.

7

9

#### 1 4. Conclusions

2

3 The selective hydrogenation of benzonitrile to benzylamine over Ni/Al<sub>2</sub>O<sub>3</sub> was discussed in 4 multiphase systems containing compressed CO<sub>2</sub>. The presence of compressed CO<sub>2</sub> retarded the 5 rate of benzonitrile conversion in solventless, hexane and ethanol, but accelerated the rate in water. The produced benzylamine was converted to carbamate and precipitated out in CO2 and 6 7 hexane-CO2 but dissolved in ethanol-CO2 and H2O-CO2 under the reaction conditions. The decreasing reaction rate with the introduction of CO<sub>2</sub> in solventless and hexane could be mainly 8 ascribed to the product benzylamine was transformed to carbamate and precipitated out and coated 9 10 on the surface of catalyst, but the decreasing reaction rate in ethanol was mainly due to the 11 dilution effect with the introduction of CO<sub>2</sub>. The increasing reaction rate in water was ascribed to 12 the enhanced concentrations of gaseous reactant H<sub>2</sub> and benzonitrile in H<sub>2</sub>O brought by CO<sub>2</sub>. 13 While, by contrasting, the yield of benzylamine in solventless, hexane and ethanol increased in the 14 presence of compressed CO2, and it reached to above 94.4% in these solvents, which was ascribed 15 to the formation of carbamate could prevent the formation of dibenzylamine. However, the yield 16 of benzylamine decreased in water with the introduction of CO<sub>2</sub>, the acidic nature of H<sub>2</sub>O-CO<sub>2</sub> 17 should be the main factor which could accelerate the hydrolysis and the elimination of NH<sub>3</sub> thus 18 reduced the yield of the main product.

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- 14

### 1 Graphical abstract





### 1 Highlights

2 3

► The addition of CO<sub>2</sub> remarkably affected the reaction rate and product selectivity.

- 4 ► The decreased reaction rate is due to the formation of solid carbamate in the presence of  $CO_2$ .
- The yield of benzylamine was increased to > 94.4% in the presence of CO<sub>2</sub>.
- 7 The presence of  $CO_2$  could prohibit the formation of dibenzylamine in organic 8 solvents.
- 9 The acidic nature of  $H_2O-CO_2$  benefited the elimination of  $NH_3$ .
- 10