Applied Catalysis A: General 455 (2013) 8–15

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

The effect of water on the hydrogenation of *o*-chloronitrobenzene in ethanol, *n*-heptane and compressed carbon dioxide

Haiyang Cheng[a,b], Xiangchun Meng[c], Yancun Yu[a,b], Fengyu Zhao[a,b,*]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[c] School of Chemical Engineering, Changchun University of Technology, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 17 January 2013
Accepted 20 January 2013
Available online 9 February 2013

Keywords:
o-chloronitrobenzene
Hydrogenation
Water
Compressed carbon dioxide

ABSTRACT

Water as a clean solvent and promoter in the organic synthesis have attracted more attention, herein the effect of water was studied for the hydrogenation of *o*-chloronitrobenzene (*o*-CNB) over Pt/C and Pd/C catalysts in ethanol, *n*-heptane and compressed CO_2. Very interesting, the reaction rate decreased in ethanol, but increased in *n*-heptane and compressed CO_2 with the addition of water. The role of water in the reaction was mainly discussed from the experimental data and phase behavior analysis, one is to activate the functional group of NO_2 through the interactions via a hydrogen bonding, and the other is to affect the solubility of hydrogen in ethanol and *n*-heptane. The positive effect of the interaction between water and reactants may be counteracted by the negative effect of hydrogen solubility in ethanol. However, the concentration of *o*-CNB and hydrogen changed slightly in *n*-heptane with the addition of water, so the interaction of water with reactants may play a main role in improving the TOF. The combination of H_2O and CO_2 is more efficient than the pure H_2O, CO_2 and H_2O–*n*-heptane systems. The phase behavior may play important role also for the improved activity except for the interactions of H_2O and CO_2 with the reactants. *o*-CNB phase was expanded in the compressed CO_2 and so the concentration of H_2 in *o*-CNB phase increased due to the miscible of CO_2 and H_2, resulting in the enhancement of reaction rate and the maximum conversion at pressure of 9 MPa CO_2, at which the volume was expanded to the largest one. The similar results were also obtained in the compressed CO_2 system without H_2O. In addition, the stability of Pt/C and Pd/C was studied in H_2O–*n*-heptane and H_2O–CO_2. As a result, the H_2O–CO_2 media and Pt/C catalyst is one of the most effective systems for the hydrogenation of *o*-CNB.

1. Introduction

Water is the most abundant, cheap, safe and environmental friendly solvent in nature and the study of organic reactions in aqueous solvents is an important theme of current research [1–3]. High reaction rate and product selectivity was reported to be obtained in some organic reactions in pure water [4–10], particularly for some cases of the organic reactants are insoluble in the aqueous phase ("on water") [2,11–16]. In addition, the use of water as solvent has the common advantages including simple separation of organic product and safe operation owing to its high heat capacity and unique redox stability. In the hydrogenation of nitroaromatics, the positive effect of water has been reported in literature [17–23], for example, water addition remarkably promotes the selective hydrogenation of CNB in ethanol over SiO_2 supported Ru, Fe, Co, Ni, Cu and Ag catalysts [21], and Ru/MgF_2 [22] and Ir/ZrO_2·xH_2O [23]. In contrast, the presence of more than 10% of water in ethanol slowed down the rate of nitrobenzene hydrogenation over Pt/Pt_2O as reported by Adams et al. [24]. Recently, Laniri et al. reported that the activities in water were greater than those in a biphasic medium consisting of water and toluene (1:1) in the hydrogenation of CNBs over a water-soluble polymer protected platinum carbonyl cluster [16]. The effects of H_2O are contradictory in the hydrogenation of nitroaromatics and the reasons are still unclear.

Supercritical carbon dioxide ($scCO_2$) is an attractive environmentally benign reaction medium in comparison with conventional organic solvents, due to its nonflammability, relative inertness, complete miscibility with gases, and easy separation from liquid/solid products [25,26]. Furthermore, $scCO_2$ can show interesting effects on reaction rates and product selectivity [26–39], which was ascribed to the interaction of compressed CO_2 with reacting species (i.e., nitrobenzene, nitrosobenzene, and

* Corresponding author at: State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, PR China. Tel.: +86 431 8526 2410; fax: +86 431 8526 2410.
E-mail address: zhaofy@ciac.jl.cn (F. Zhao).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.01.028

N-phenylhydroxylamine) [27–29] and modification of the catalyst surface with CO generated from CO_2 hydrogenation [35]. Compared with pure $scCO_2$ or H_2O solvent, the combination of CO_2 and H_2O is more beneficial for selective hydrogenation of water-insoluble organic compounds [29,32,40–42]. Recently, the present authors had studied the hydrogenation of nitrobenzene (NB) and CNB over supported Ni catalysts in H_2O–CO_2. We found the reaction rate was higher in H_2O–CO_2 than those in H_2O or $scCO_2$, and the selectivity to aniline and chloroaniline (CAN) reached about 100% in the whole range of conversion for the reactions in H_2O–CO_2 and $scCO_2$ [29]. However, the deactivation of catalyst was serious, especially in H_2O–CO_2.

In present work, we studied the effect of water on the hydrogenation of *o*-CNB over Pt/C and Pd/C in ethanol, *n*-heptane and compressed CO_2. In addition, the effect of CO_2 pressure on the conversion and selectivity was also studied and discussed in detail, and the results difference to the previous Ni/TiO_2 catalyst was discussed from the phase behavior and the catalyst hydrophilic properties. The Pt/C catalyst was demonstrated to be effective and stable for the hydrogenation of *o*-CNB in H_2O–CO_2.

2. Experimental

2.1. Chemicals

5 wt% Pd/C and 5 wt% Pt/C catalysts were purchased from WAKO and used as received. Ethanol, *n*-heptane and *o*-CNB from Beijing Chemical Reagent Cooperation, are of analytical grade and used without further purification. The water was deionized water. Gases of H_2 (99.999%), N_2 (99.999%) and CO_2 (99.999%) were used as delivered.

2.2. Catalyst characterization

The average size of Pd and Pt crystalline particles was estimated by X-ray diffraction (XRD) pattern recorded on D8 ADVANCE X-ray Diffractometer, and calculated by the Debye–Scherer formula. X-ray photoelectron spectroscopy (XPS, VG Microtech 3000 Multilab) was used to examine the electronic properties of Pt and Pd on the surface of the Pt/C and Pd/C catalysts. The C 1s peak at 284.6 eV arising from adventitious carbon was used as reference. This reference gives binding energy values with a precision of ±0.2 eV. The surface composition of the samples was determined from the peak areas of the corresponding lines using a Shirley type background and empirical cross section factors for XPS. The fresh catalysts were characterized directly. The used catalysts, prior to characterization, were washed thoroughly with ethanol for 6 times, separated by centrifugation, and dried in vacuum at 60 °C overnight. The leaching of Pt and Pd into solvents was measured by ICP-OES (iCAP6300, Thermo USA).

2.3. Hydrogenation reaction

The hydrogenation of *o*-CNB was carried out in a 50 ml high-pressure stainless steel batch reactor. In a typical experiment, catalyst (5 mg), *o*-CNB (1.5 g) and deionized water (10 ml) were loaded into the reactor. Then the reactor was sealed and flushed three times with N_2 to remove air, and heated to the reaction temperature of 35 °C. Hydrogen (4 MPa) and then liquid CO_2 was introduced into the reactor using a high-pressure liquid pump to the desired pressure. The reaction mixture was stirred continuously with a magnetic stirrer during reaction. The stirring speed was 1200 rpm to make sure that the reaction was free from any significant mass transport limitations. After reaction the reactor was cooled in ice-water bath, depressurized carefully, and the liquid product was extracted with *n*-hexane/diethyl ether (v/v = 1/1) and analyzed with a gas chromatograph (GC-Shimadzu-2010, FID, Capillary column, Rtx-5 30 m × 0.25 mm × 0.25 μm), and identified by gas chromatography/mass spectrometry (GC/MS, Agilent 5890, FID, Capillary column, HP 5). The GC results were obtained using an internal standard method and biphenyl was always used as internal standard. Hydrogenation reactions in H_2O, $scCO_2$, *n*-heptane, H_2O–*n*-heptane, ethanol and H_2O–ethanol were conducted in the same reactor using similar procedures. For recycling experiment in H_2O–*n*-heptane, the reaction mixture of the first run was separated by decantation, and then the solid catalysts were washed three times with *n*-heptane and reused. The next run was started with the fresh *o*-CNB and *n*-heptane. For recycling experiment in H_2O–CO_2, the reaction mixture of the first run was extracted by $scCO_2$, and the solid catalyst and water were reused for the next run with adding fresh *o*-CNB, and reaction was started under the similar conditions.

2.4. Visual observation of the phase behavior in H_2O–CO_2

The observation of the phase state of *o*-CNB in H_2O–CO_2 was carried out in an 85 ml high-pressure view cell. Water (17 ml) and *o*-CNB (2.55 g) were added and the reactor was heated up to 35 °C, H_2 (4 MPa) and then liquid CO_2 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.

3. Results and discussion

3.1. Catalytic performances of Pd/C and Pt/C in different reaction media

Table 1 shows the results of hydrogenation of *o*-CNB over Pd/C in different reaction systems. The turnover frequency (TOF) in ethanol ($28.5\ s^{-1}$) was much higher than that in H_2O ($11.0\ s^{-1}$) (entries 1, 6), but it was lowered down ($17.2\ s^{-1}$) by introducing water (entry 7). The selectivity to *o*-CAN was < 90% in ethanol and H_2O–ethanol due to the dechlorination and the accumulation of intermediates (*o*-chloronitrosobenzene (CNSB), *N*-chloro-phenylhydroxylamine (CPHA), dichloroazoxybenzene (CAOB), dichloroazobenzene (CAB), and dichlorohydrazobenzene (CHAB)) (entries 6–10). In H_2O, it reached to 98.6% and did not change much with extending reaction time at complete conversion (entries 4, 5). The TOF in *n*-heptane ($9.79\ s^{-1}$) was slightly lower than that in H_2O ($11.0\ s^{-1}$) (entries 1, 11), but it was enhanced to $15.3\ s^{-1}$ by introducing water into *n*-heptane (entry 12), and further enhanced by introducing less amount of water into *n*-heptane (entry 13, 14). In H_2O–*n*-heptane, the selectivity to *o*-CAN reached to 99.5% at complete conversion of *o*-CNB and did not change much with extending reaction time because the dechlorination and the accumulation of intermediates was low in a conversion range of 50–100% (entries 14–17). The TOF in 9 MPa CO_2 ($4.3\ s^{-1}$) was lower than that in H_2O ($11.0\ s^{-1}$) (entries 1, 18), but it was improved ($19.9\ s^{-1}$) in the H_2O–9 MPa CO_2 system (entry 23). The time needed for a complete conversion in H_2O–CO_2 (65 min) was much short than that in H_2O (120 min) and $scCO_2$ (360 min) (entry 3, 20, 25). At complete conversion, the selectivity to *o*-CAN in H_2O–CO_2 (99%) was higher than that in H_2O (98.5%) and $scCO_2$ (95.5%) (entries 5, 22, 25), due to that the dechlorination and the accumulation of intermediates (CNSB, AOB, AB, and HAB) were fully inhibited in H_2O–CO_2, and it did not change much with extending reaction time (entry 26).

For Pt/C catalyst (Table 2), the TOF in ethanol ($87.3\ s^{-1}$) was much higher than that in H_2O ($6.95\ s^{-1}$) (entries 1, 2), but it was slightly decreased to $85.4\ s^{-1}$ by introducing water into ethanol

Table 1
Hydrogenation of *o*-CNB over 5% Pd/C in various media.

Entry	Medium	Time (min)	Conversion (%)	Selectivity (%)			TOF[a] (s^{-1})
				o-CAN	Dechlo.[b]	Others[c]	
1	10 ml H_2O	25	28	87.8	1.4	10.8	11.0
2		60	55	89.3	1.2	9.5	8.96
3		120	99	96.5	1.2	2.3	8.07
4		180	100	98.6	1.2	0.2	–
5		260	100	98.5	1.5	–	–
6	10 ml ethanol	25	73	78.7	3.9	17.4	28.5
7	2 ml H_2O + 8 ml ethanol	25	44	70.7	6.1	23.2	17.2
8		60	99	78.8	5.9	15.3	16.1
9		120	100	86.9	7.2	5.9	–
10		180	100	88.4	11.0	0.6	–
11	10 ml *n*-heptane	25	25	95.0	0.5	4.5	9.79
12	10 ml H_2O +10 ml *n*-heptane	25	39	94.5	0.8	4.7	15.3
13	6 ml H_2O + 10 ml *n*-heptane	25	45	95.2	0.8	4.0	17.6
14	2 ml H_2O + 10 ml *n*-heptane	25	50	97.4	0.7	1.9	19.6
15		65	98	98.9	0.5	0.6	14.7
16		120	100	99.5	0.5	–	–
17		180	100	99.3	0.7	–	–
18	9 MPa CO_2	25	11	86.0	2.0	12.0	4.30
19		240	81	76.2	0.2	23.6	3.30
20		360	99	89.9	0.6	9.5	2.69
21		480	100	92.5	0.5	7.0	–
22		600	100	95.5	0.6	3.9	–
23	10 ml H_2O + 9 MPa CO_2	25	51	94.1	1.2	4.7	19.9
24		50	92	96.8	0.6	2.6	18.0
25		65	100	99.0	0.7	0.3	–
26		120	100	99.0	1.0	–	–

Reaction conditions: 5 mg 5% Pd/C, 9.52 mmol *o*-CNB, 4 MPa H_2, 35 °C.

[a] Turnover frequency; which was given as the overall rate of *o*-CNB conversion normalized by the number of active sites over the specified time. The number of active sites was calculated by (the metal dispersion) × (the total number of supported metal atoms). The Pd dispersion (D) was calculated from the following equation: Dispersion = $6(\nu_m/a_m)/d$, where ν_m and a_m are equal to 14.70 Å^3 and 7.93 Å^2, respectively, and the average diameter (d) of Pd particles was determined to be 16.1 nm by XRD measurements.

[b] By-products from dechlorination are aniline and nitrobenzene.

[c] Intermediates include *o*-chloronitrosobenzene, dichloroazoxybenzene, dichloroazobenzene, and dichlorohydrazobenzene.

(entry 3). The TOF in *n*-heptane (41.7 s^{-1}) was much higher than that in H_2O (6.95 s^{-1}) (entries 1, 4), and it was slightly enhanced (42.7 s^{-1}) by introducing water into *n*-heptane (entry 6). The selectivity to *o*-CAN in H_2O-*n*-heptane was higher than that in *n*-heptane at complete conversion of *o*-CNB (entries 5, 7). The TOF in 9 MPa CO_2 (34.4 s^{-1}) was much higher than that in H_2O (6.95 s^{-1}) (entries 1, 8), and was further enhanced (45.0 s^{-1}) in the H_2O–9 MPa CO_2 system (entry 14). The conversion and selectivity to *o*-CAN increased

Table 2
Hydrogenation of *o*-CNB over 5% Pt/C in various media.

Entry	Medium	Time (min)	Conversion (%)	Selectivity (%)			TOF[a] (s^{-1})
				o-CAN	Dechlo.[b]	Others[c]	
1	10 ml H_2O	25	35	81.4	1.2	17.4	6.95
2	10 ml ethanol	5	88	70.6	0.8	28.6	87.3
3	2 ml H_2O + 8 ml ethanol	5	86	61.6	0.9	37.5	85.4
4	10 ml *n*-heptane	5	42	79.1	1.6	19.3	41.7
5		25	100	91.5	2.2	6.3	–
6	10 ml H_2O + 10 ml *n*-heptane	5	43	83.5	0.4	17.2	42.7
7		25	100	96.2	0.5	3.3	–
8	9 MPa CO_2	7.5	52	61.8	0.3	37.9	34.4
9		15	87	68.0	0.5	31.5	28.8
10		25	99	74.0	0.6	25.4	19.7
11		60	100	80.8	0.6	18.6	–
12		180	100	90.6	0.3	9.1	–
13		300	100	99.0	0.6	0.4	–
14	10 ml H_2O + 9 MPa CO_2	7.5	68	62.8	0.2	37.0	45.0
15		15	95	61.6	0.1	38.3	31.4
16		25	100	69.7	0.1	30.2	–
17		120	100	83.7	0.2	16.1	–
18		240	100	97.5	0.3	2.2	–
19		300	100	99.5	0.3	0.2	–

Reaction conditions: 5 mg 5% Pt/C, 9.52 mmol *o*-CNB, 4 MPa H_2, 35 °C.

[a] Turnover frequency; which was given as the overall rate of *o*-CNB conversion normalized by the number of active sites over the specified time. The number of active sites was calculated by (the metal dispersion) × (the total number of supported metal atoms). The Pt dispersion (D) was calculated from the following equation: Dispersion = $6(\nu_m/a_m)/d$, where ν_m and a_m are equal to 15.10 Å^3 and 8.07 Å^2 respectively, and the average diameter (d) of Pt particles was determined to be 4.5 nm by XRD measurements.

[b] By-products from dechlorination are aniline and nitrobenzene.

[c] Intermediates include *o*-chloronitrosobenzene, dichloroazoxybenzene, dichloroazobenzene, and dichlorohydrazobenzene.

with extending reaction time, and the selectivity to dechlorination byproducts was lower than 0.6% in 9 MPa CO_2 and H_2O–CO_2 (entries 8–19); the selectivity to *o*-CAN reached to 99.0% in 9 MPa CO_2 and 99.5% in H_2O–CO_2 at complete conversion of *o*-CNB (entries 13, 19).

The addition of 20% water to ethanol had negative effect on the conversion of *o*-CNB over Pd/C and Pt/C catalysts, although water, ethanol and *o*-CNB are miscible and catalyst was uniformly dispersed in the mixture under the conditions. The effect of water may be considered from the following two factors (a) the interactions of water with the reacting species (i.e., *o*-CNB, *o*-CNSB, and CPHA) and (b) solubility of hydrogen and *o*-CNB in the solution. It was reported that hydrogen bonds were formed intermolecular of NB and H_2O that protrude farthest into the organic phase through molecular dynamics study of the H_2O/NB interface [43,44]. The N—O bond of PHA is weakened through interaction with H_2O as confirmed by FTIR results [29], possibly via OH···O and OH···N bonding [45]. These interactions may also exist between *o*-CNB, *o*-CNSB, *o*-CHPA and H_2O, and could be favorable to the hydrogenation of —NO_2, —NO and —NHOH groups. The solubility of hydrogen changed with the composition of H_2O–ethanol and it decreased markedly with increase of water volume in ethanol. For example, the solubility of hydrogen decreased about 40% when 20% of water was introduced into ethanol [17]. When increase of both the amount of catalyst and the water content, the rate determining step may change from the surface catalytic reaction to the mass transfer of hydrogen [17]. Herein, for Pd/C and Pt/C catalyst, the solubility of hydrogen in the solvent may play the main role in controlling the reaction rate. The positive effect of the interaction between H_2O and reactants may be counteracted by the negative effect of hydrogen solubility with increasing water content in ethanol.

Laniri et al. reported that the activities in H_2O were greater than those in a biphasic medium consisting of H_2O and toluene (1:1) in the hydrogenation of CNBs over water-soluble polymer protected platinum carbonyl cluster, owing to that the catalyst was dispersed in aqueous phase and the concentrations of dissolved CNBs in the aqueous phase in pure H_2O were higher than those in H_2O–toluene biphasic medium [16]. However, in the present results, over Pd/C and Pt/C, the activity in *n*-heptane and H_2O was lower than that in a biphasic medium consisting of H_2O and *n*-heptane (1:1). Pd/C and Pt/C were hydrophobic and mainly dispersed in *n*-heptane, and the concentrations of *o*-CNB and hydrogen in *n*-heptane did not change much, so the interactions of H_2O with the reacting species should play an important role in the improved TOF in H_2O–*n*-heptane. The activity in 9 MPa CO_2 and H_2O was also lower than that in H_2O–9 MPa CO_2 biphasic medium, which may be due to the interactions of H_2O and CO_2 with the reacting species, and will be described in detail below.

3.2. Influence of CO_2 pressure and phase behavior

Biphasic system especially H_2O–CO_2 medium is more effective for the selective hydrogenation of *o*-CNB and inhibits the dechlorination. CO_2 pressure exerted a significant effect on the conversion, as shown in Fig. 1. In the H_2O–CO_2 system, with CO_2 pressure up to 9 MPa, the conversion increased from 45% to 92% for Pd/C and increased from 23% to 95% for Pt/C catalysts, but it decreased with the further increasing of CO_2 pressure (Fig. 1a, b). In the compressed CO_2 system, with CO_2 pressure up to 9 MPa, the conversion increased from 43% to 87% for Pt/C catalyst, and it decreased also with the further increasing of CO_2 pressure (Fig. 1c).

The phase behavior, and the concentration of *o*-CNB and hydrogen in the liquid and CO_2 phases might be important factors in determining the rate of *o*-CNB hydrogenation. Under the reaction conditions, as shown in Fig. 2, three phases of gas CO_2, H_2 and dissolved *o*-CNB, liquid *o*-CNB (*o*-CNB, dissolved H_2 and CO_2) and liquid H_2O presented at the CO_2 pressure below 17.4 MPa, and then

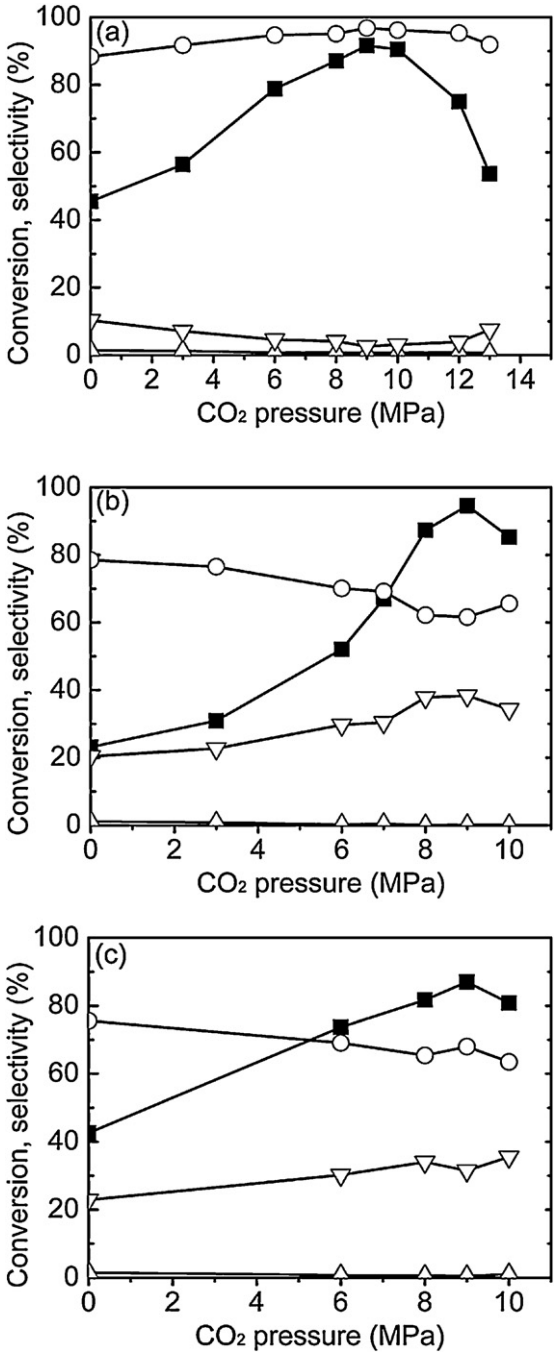

Fig. 1. Influence of CO_2 pressure on the conversion (■) and the selectivity for the hydrogenation of *o*-CNB. (a) 5% Pd/C in H_2O, (b) 5% Pt/C in H_2O, and (c) 5% Pt/C in pure CO_2. Reaction conditions: 1.5 g *o*-CNB, 5 mg catalyst, 4 MPa H_2, 10 ml H_2O, 35 °C, 50 min for 5% Pd/C and 15 min for 5% Pt/C. (○) *o*-CAN, (△) aniline and nitrobenzene, (▽) intermediates include *o*-chloronitrosobenzene, dichloroazoxybenzene, dichloroazobenzene, and dichlorohydrazobenzene.

two phases of gas (CO_2, H_2 and dissolved *o*-CNB) and liquid H_2O at pressure of CO_2 beyond 17.4 MPa were observed. The *o*-CNB volume was expanded with increasing of CO_2 pressure and the maximum volume was obtained at 9 MPa (Fig. 2b). A certain amount of *o*-CNB dissolved into the CO_2 phase with the further increasing of CO_2 pressure, and the *o*-CNB phase disappeared at 17.4 MPa (Fig. 2c). In the absence of H_2O, the *o*-CNB volume was expanded with increasing of CO_2 pressure and the maximum volume was also obtained at 9 MPa (Fig. 3b), however, a completely miscible mixture (*o*-CNB, H_2 and CO_2) was formed at 12.3 MPa CO_2 (Fig. 3c). In other words,

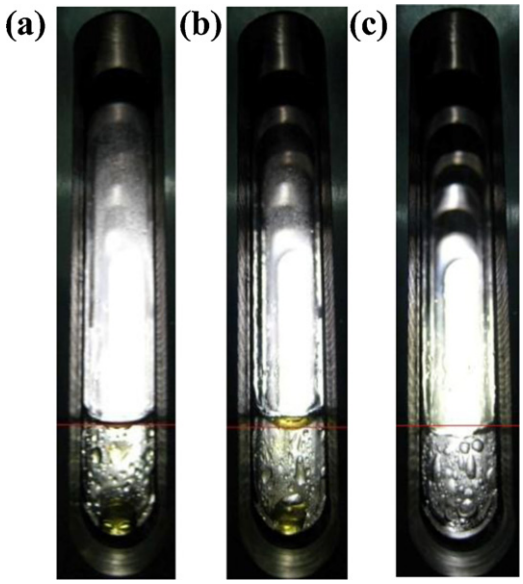

Fig. 2. Visual observations of the reaction mixture including *o*-CNB, H_2O, H_2, and CO_2 at 35 °C and at CO_2 pressures given (a) 0.1 MPa, (b) 9 MPa, (c) 17.4 MPa. Conditions: viewing cell volume 85 ml, 17 ml H_2O, 2.55 g *o*-CNB, 4 MPa H_2.

the higher CO_2 pressure was needed to dissolve *o*-CNB completely into CO_2 gas phase in the presence of H_2O, and this indicates the presence of interaction between H_2O and *o*-CNB.

Fig. 4 illustrates the processes for catalytic reaction and catalyst–product separation. Pd/C and Pt/C were hydrophobic catalysts and mainly disperse in *o*-CNB under stirring, the mass-transfer resistance between gas (H_2) and *o*-CNB droplet decreased with increasing of CO_2 pressure [38], so the reaction rate increased with CO_2 pressure in H_2O–CO_2 system. However, with the further increasing of CO_2 pressure, *o*-CNB was gradually extracted into $scCO_2$ phase, resulting in the decrease of *o*-CNB concentration in the liquid phase and the reaction rate decreased at pressure beyond 9 MPa CO_2. The maximum conversion was obtained at 9 MPa CO_2

Fig. 3. Visual observations of the reaction mixture including *o*-CNB, H_2, and CO_2 at 35 °C and at CO_2 pressure given (a) 0.1 MPa, (b) 9 MPa, (c) 17.4 MPa. Conditions: viewing cell volume 74 ml, 2.22 g *o*-CNB, 4 MPa H_2.

for both Pd/C and Pt/C catalysts, and which increased 2 and 4 times compared to the value at 0.1 MPa CO_2 (Fig. 1a, b). In our previous work, however, the maximum conversion was obtained at 13 MPa CO_2 for Ni/TiO_2 catalyst at similar reaction conditions in H_2O–CO_2 system [29]. The maximum conversion presented at different CO_2 pressure was ascribed to the different properties of catalyst; Ni/TiO_2 catalyst is hydrophilic and mainly dispersed in water as shown in Fig. 5. *o*-CNB is partially soluble in CO_2 and CO_2 can partially soluble in H_2O [46], so the dissolution of CO_2 in H_2O can enhance the concentration of H_2 and *o*-CNB in H_2O phase and thus resulting in an enhancement of the reaction rate with increasing of CO_2 pressure. The maximum conversion presented at 13 MPa, at which the concentration of *o*-CNB in H_2O reached maximum. However, *o*-CNB could be gradually extracted into $scCO_2$ phase at the quite high pressure of CO_2 (>17.4 MPa), resulting in the decrease of *o*-CNB concentration in the aqueous phase, and so the reaction rate was decreased. But for the Pd/C and Pt/C catalysts, they are hydrophobic and mainly disperse in *o*-CNB phase (Fig. 4), with increasing of CO_2 pressure the CO_2 expanded liquid phase was formed (Fig. 2). The maximum conversion was obtained at 9 MPa in H_2O–CO_2 (Fig. 1b), at which the liquid phase was expanded maximum and the concentrations of H_2 and *o*-CNB in the liquid phase reached the largest value.

Moreover, the higher activity in H_2O–CO_2 can be explained by some factors. The acidic nature of the H_2O–CO_2 might be one of positive factors, but its effect is negligible [29]. The hydrogen bonding between water and the reacting species as described above may be an important factor. Interfacial hydrogen bonding of OH···ONO formed between H_2O and NB molecules [47], which may weaken the N—O bond. Previously, a striking rate increase was observed in some reactions on H_2O and this was ascribed to the hydrogen bonds between interfacial H_2O molecules and reactants or transition states [48]. In addition, our previous in situ FTIR showed that compressed CO_2 interacts with the reacting species, CNB, CNSB, and CPHA, decreasing the reactivity of CNB but increasing the reactivity of CNSB and CPHA [28]. These molecular interactions should also be important in the H_2O–CO_2–*o*-CNB reaction system.

The presence of CO_2 is helpful to suppress the dechlorination reactions of *o*-CNB and *o*-CAN over Pd/C and Pt/C in H_2O–CO_2. It was consistent with previous results [28,29,35,39] that CO generated from CO_2 hydrogenation could act as a modifier for Pt/C catalyst to block the active sites for dechlorination in $scCO_2$ [35].

3.3. Recycling of catalysts

The recycling of catalyst has been examined with Pd/C and Pt/C in H_2O–*n*-heptane and H_2O–CO_2 (Table 3). For Pd/C, the deactivation was obvious in H_2O–*n*-heptane and more serious in H_2O–CO_2. For Pt/C, the activity changed little in H_2O–*n*-heptane but decreased slightly in H_2O–CO_2, in these systems the similar selectivity was obtained after five recycles. ICP analysis was used to investigate the possibility of Pd and Pt leaching during the reaction in H_2O–*n*-heptane and H_2O–CO_2. Pd and Pt was not detected in filtrate due to the concentration was lower than the detection limit (0.1 ppm), it suggested that the leaching of Pd and Pt was negligible even though the H_2O–CO_2 reaction system presents somewhat acidity (ca. pH 3 [49]).

Since deactivation of supported catalysts usually relates with agglomeration of metal particles, the change of the particle sizes before and after reaction in H_2O–CO_2 was examined with XRD (Fig. 6). The average Pd and Pt particle sizes were 16.1 and 4.5 nm, respectively, and did not change after reaction. Therefore, the agglomeration of Pd and Pt particles were not the main factor to cause the deactivation of catalysts.

XPS was used to investigate the electronic state of Pd and Pt on the surface of the fresh and used catalysts. As shown in Fig. 7,

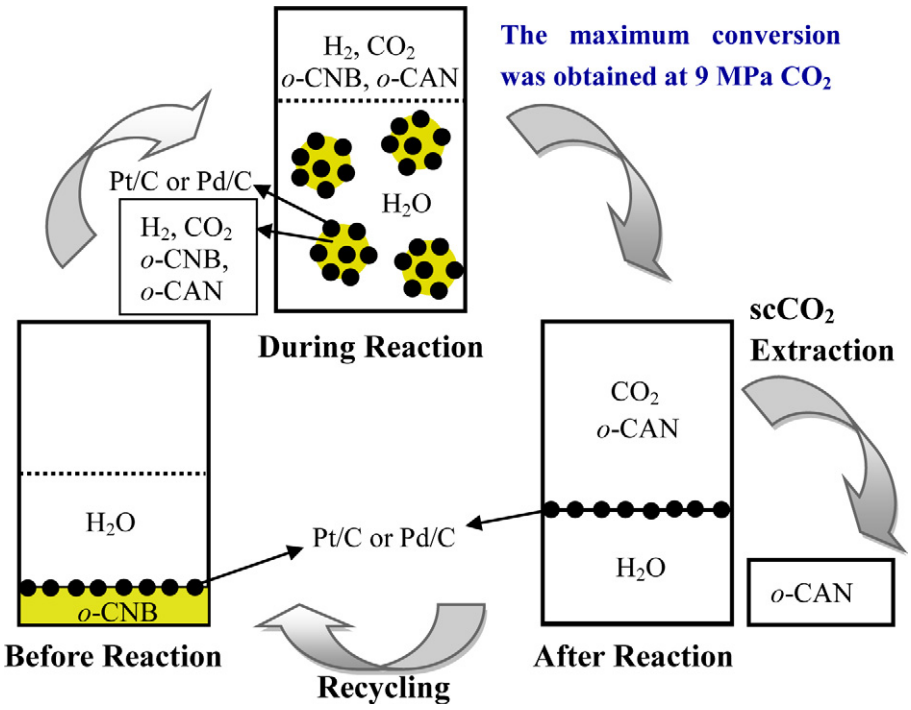

Fig. 4. Reaction, separation, and recycling processes for the hydrogenation of *o*-CNB over Pt/C or Pd/C catalyst under gas (H_2, CO_2)–liquid (H_2O) conditions.

for Pd/C catalyst, the peaks with binding energy of Pd $3d_{3/2}$ at 340.3 eV and Pd $3d_{5/2}$ at 335.0 eV are characteristic of Pd^0, and the peaks with binding energy of Pd $3d_{3/2}$ at 342.2 eV and Pd $3d_{5/2}$ at 337.0 eV are characteristic of Pd^{2+} [50]. The atomic ratios of Pd^{2+}/Pd^0 were 0.38 and 1.73 for the fresh and the used Pd/C catalysts in H_2O–CO_2, respectively, indicating that the oxidization of Pd species was responsible for the deactivation of Pd/C during the hydrogenation of *o*-CNB. The oxidized Pd species may be amorphous, so no reflections associated with them were observed in the XRD patterns of the Pd/C catalyst. For the fresh Pt/C catalyst, the peaks with binding energy of Pt $4f_{5/2}$ at 74.5 eV and $Pt4f_{7/2}$ at 71.0 eV are characteristic of Pt^0. For the used Pt/C catalyst in H_2O–CO_2, only two peaks corresponding to Pt^0 were found, which are similar to the fresh catalyst; so Pt/C was much more stable than Pd/C in H_2O–CO_2.

The deactivation of Pd/C catalyst was more serious in H_2O–CO_2 than that in H_2O–*n*-heptane (Table 3). The deactivation of Au/TiO_2 catalyst in the hydrogenation of *o*-CNB in the presence of CO_2 was

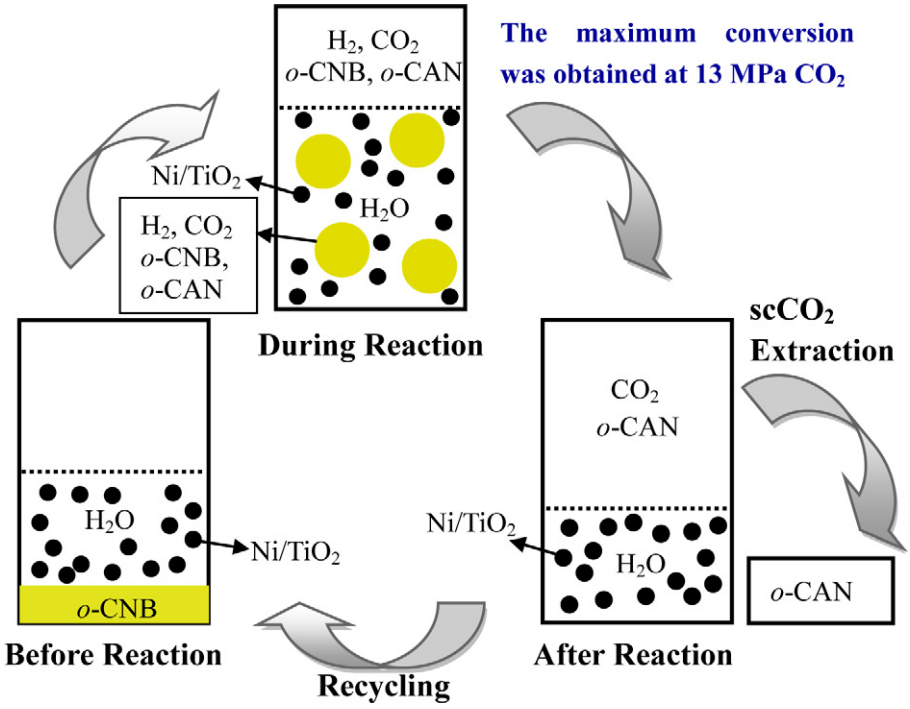

Fig. 5. Reaction, separation, and recycling processes for the hydrogenation of *o*-CNB over Ni/TiO_2 catalyst under gas (H_2, CO_2)–liquid (H_2O) conditions.

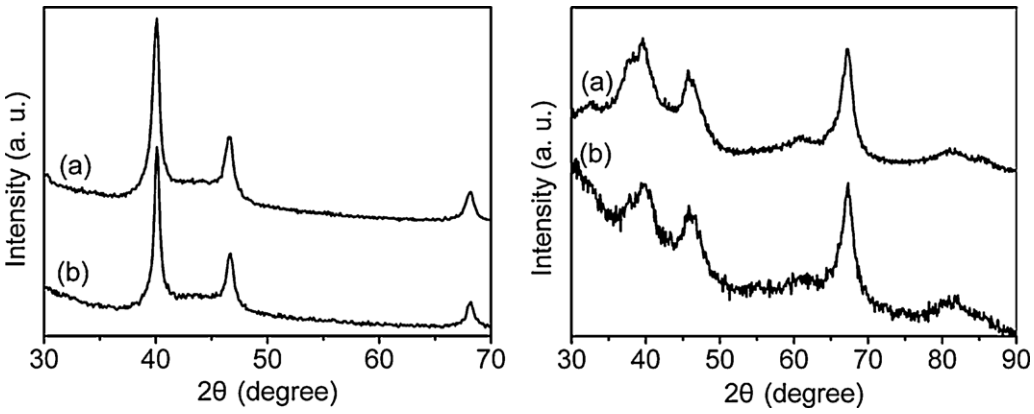

Fig. 6. XRD patterns of 5% Pd/C (left) and 5% Pt/C (right), (a) before reaction (b) after reaction in H_2O–CO_2.

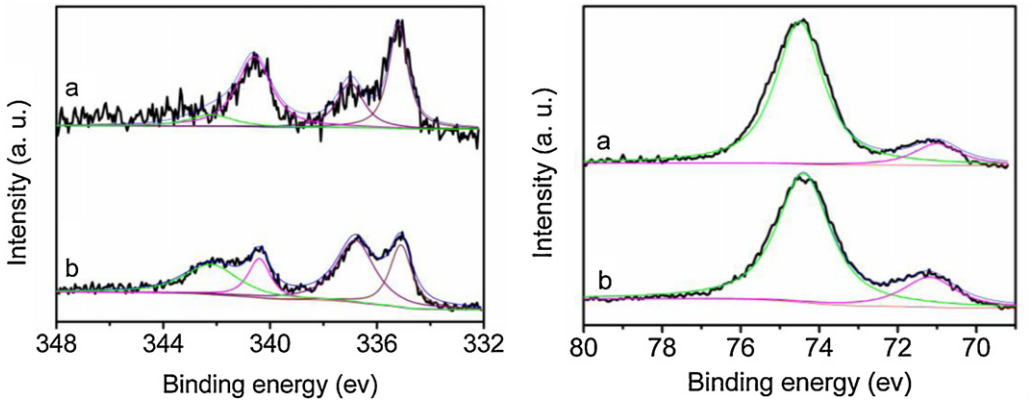

Fig. 7. XPS spectra of 5% Pd/C (left) and 5% Pt/C (right), (a) before reaction and (b) after reaction in H_2O–CO_2.

ascribed to the carbonate-like species forming on the surface of Au/TiO_2 and the original Au^0 species partially oxidized by CO_2 [51]. Herein, the oxidization of Pd species was also presented in H_2O–CO_2, CO might be generated from CO_2 during the hydrogenation process and poisoned some active sites [35], and it may be more serious for Pd/C. It is worth noting that the Pt/C, CO_2 and H_2O phase were easily separated from the organic product phase after the reaction. Hence, they are recyclable without any post purification, the H_2O–CO_2 and Pt/C catalyst system is effective for practical production of *o*-CAN from the hydrogenation of *o*-CNB.

Table 3
Results of the catalyst recycling test in the hydrogenation of *o*-CNB over 5% Pd/C and 5% Pt/C in H_2O–*n*-heptane and H_2O–CO_2.

Catalyst	Run	Conversion (%)	Selectivity (%)		
			o-CAN	AN	Others
In H_2O–*n*-heptane					
Pd/C	1	98	98.9	0.5	0.6
	2	78	96.7	0.5	2.8
	3	58	95.9	0.9	3.2
Pt/C	1	90	89.5	0.3	10.2
	2	90	89.6	0.3	10.1
	3	91	89.6	0.2	10.2
	4	92	89.3	0.3	10.4
	5	91	84.3	0.3	15.4
In H_2O–CO_2					
Pd/C	1	100	99.0	0.7	0.3
	2	30	83.5	2.9	13.6
	3	12	83.3	1.9	14.8
Pt/C	1	100	76.9	0.3	22.8
	2	99	80.9	0.2	18.9
	3	97	79.2	0.2	20.6
	4	93	84.1	0.2	15.7
	5	91	81.9	0.3	17.8

Reaction condition: 5 mg 5%Pd/C or 5% Pt/C, 9.52 mmol *o*-CNB, 4 MPa H_2, 35 °C. In H_2O–*n*-heptane: 2 ml H_2O, 10 ml *n*-heptane, 65 and 15 min of reaction over Pd/C and Pt/C, respectively. In H_2O–CO_2: 10 ml H_2O, 9 MPa CO_2, 65 and 25 min of reaction over Pd/C and Pt/C, respectively.

4. Conclusions

The effects of water on the hydrogenation of *o*-CNB over Pt/C and Pd/C were studied in ethanol, *n*-heptane and compressed CO_2. The interactions of water with the reacting species and the solubility of hydrogen in liquid phase were considered to have largely influence to the reaction rate. The positive effect of interaction between H_2O and *o*-CNB by hydrogen bonding could counteract by the negative effect of hydrogen solubility in H_2O–ethanol resulting in a decrease in the TOF. While the concentrations of *o*-CNB and hydrogen changed very slightly in H_2O–*n*-heptane, so the molecular interaction played an important role in the improved TOF. Moreover, the higher TOF was obtained in H_2O–CO_2 system than that in H_2O and compressed CO_2 due to the phase behavior and the interactions among H_2O, CO_2 with CNB. In addition, the conversion over Pd/C and Pt/C in H_2O–CO_2 and pure $scCO_2$ presented the maximum values at 9 MPa, which is largely different to the results over previous Ni/TiO_2 (13 MPa). It was explained by the phase behavior and surface properties of Pd/C, Pt/C (hydrophobic) and Ni/TiO_2 (hydrophilic). The combination of H_2O and CO_2 is the most efficient and green reaction media for the present hydrogenation of CNB. However, the Pd/C catalyst deactivation was found, it deactivated faster in H_2O–CO_2 system compared to H_2O–*n*-heptane due to the changes of Pd species and the poisoning by CO generated during the reaction. Pt/C catalyst was stable in H_2O–*n*-heptane and

similar reaction rate and product selectivity was obtained after five times recycle, but it decreased slightly in H_2O–CO_2 system. The stability improvement of Pt/C catalyst will be further studied in our future work.

Acknowledgements

The authors gratefully acknowledge the financial supports from NSFC 21273222, 21202159 and 21143001, and from Jilin province, China 20100562.

References

[1] S. Minakata, M. Komatsu, Chem. Rev. 109 (2009) 711–724.
[2] A. Chanda, V.V. Fokin, Chem. Rev. 109 (2009) 725–748.
[3] R.N. Butler, A.G. Coyne, Chem. Rev. 110 (2010) 6302–6337.
[4] F. Joo, Aqueous Organometallic Catalysis, vol. 23, Kluwer Academic, Dordrecht, 2001.
[5] V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Ed. 40 (2001) 3455–3457.
[6] J. Morita, H. Nakatsuji, T. Misaki, Y. Tanabe, Green Chem. 7 (2005) 711–715.
[7] J.C. Mao, B.S. Wan, F. Wu, S.W. Lu, Tetrahedron Lett. 46 (2005) 7341–7344.
[8] X.L. Xu, T. Hirao, J. Org. Chem. 70 (2005) 8594–8596.
[9] N. Jiang, A.J. Ragauskas, Tetrahedron Lett. 47 (2006) 197–200.
[10] Y.Z. Xiang, L. Ma, C.S. Lu, Q.F. Zhang, X.N. Li, Green Chem. 10 (2008) 939–943.
[11] Z.M. Wang, K.B. Sharpless, J. Org. Chem. 59 (1994) 8302–8303.
[12] Z.P. Demko, K.B. Sharpless, J. Org. Chem. 66 (2001) 7945–7950.
[13] S. Narayan, J. Muldoon, M.G. Finn, V.V. Fokin, H.C. Kolb, K.B. Sharpless, Angew. Chem. Int. Ed. 44 (2005) 3275–3279.
[14] J.E. Klijn, J. Engberts, Nature 435 (2005) 746–747.
[15] N. Shapiro, A. Vigalok, Angew. Chem. Int. Ed. 47 (2008) 2849–2852.
[16] P. Maity, S. Basu, S. Bhaduri, G.K. Lahiri, Adv. Synth. Catal. 349 (2007) 1955–1962.
[17] H.C. Yao, P.H. Emmett, J. Am. Chem. Soc. 81 (1959) 4125–4132.
[18] H.C. Yao, P.H. Emmett, J. Am. Chem. Soc. 83 (1961) 796–799.
[19] K. Taya, Sci. Pap. I.P.C.R. 56 (1962) 285–289.
[20] S. Nishimura, Handbook of heterogeneous catalytic hydrogenation for organic synthesis, John Wiley & Sons, Inc., New York, 2001, 334.
[21] J. Ning, J. Xu, J. Liu, H. Miao, H. Ma, C. Chen, X. Li, L. Zhou, W. Yu, Catal. Commun. 8 (2007) 1763–1766.
[22] M. Pietrowski, M. Zielinski, M. Wojciechowska, Catal. Lett. 128 (2009) 31–35.
[23] G.Y. Fan, L. Zhang, H.Y. Fu, M.L. Yuan, R.X. Li, H. Chen, X.J. Li, Catal. Commun. 11 (2010) 451–455.
[24] R. Adams, F.L. Cohen, O.W. Rees, J. Am. Chem. Soc. 49 (1927) 1093–1099.
[25] C.A. Eckert, B.L. Knutson, P.G. Debenedetti, Nature 383 (1996) 313–318.
[26] T. Seki, J.D. Grunwaldt, A. Baiker, Ind. Eng. Chem. Res. 47 (2008) 4561–4585.
[27] X.C. Meng, H.Y. Cheng, Y. Akiyama, Y.F. Hao, W.B. Qiao, Y.C. Yu, F.Y. Zhao, S. Fujita, M. Arai, J. Catal. 264 (2009) 1–10.
[28] X.C. Meng, H.Y. Cheng, S. Fujita, Y.F. Hao, Y.J. Shang, Y.C. Yu, S.X. Cai, F.Y. Zhao, M. Arai, J. Catal. 269 (2010) 131–139.
[29] X.C. Meng, H.Y. Cheng, S. Fujita, Y.C. Yu, F.Y. Zhao, M. Arai, Green Chem. 13 (2011) 570–572.
[30] M. Chatterjee, A. Chatterjee, H. Kawanami, T. Ishizaka, T. Suzuki, A. Suzuki, Adv. Synth. Catal. 354 (2012) 2009–2018.
[31] S. Fujita, X.C. Meng, F.Y. Zhao, M. Arai, in: M. R. Belinsky (Eds.), Supercritical Fluids. Nova Science Publishers, Inc., New York, 2010, p. 609-631.
[32] S. Fujita, S. Akihara, F.Y. Zhao, R.X. Liu, M. Hasegawa, M. Arai, J. Catal. 236 (2005) 101–111.
[33] C.M. Rayner, Org. Process Res. Dev. 11 (2007) 121–132.
[34] F.Y. Zhao, S. Fujita, S. Akihara, M. Arai, J. Phys. Chem. A 109 (2005) 4419–4424.
[35] S. Ichikawa, M. Tada, Y. Iwasawea, T. Ikariya, Chem. Commun. (2005) 924–926.
[36] F. Zhao, Y. Ikushima, M. Arai, J. Catal. 224 (2004) 479–483.
[37] F.Y. Zhao, S. Fujita, J.M. Sun, Y. Ikushima, M. Arai, Catal. Today 98 (2004) 523–528.
[38] F.Y. Zhao, R. Zhang, M. Chatterjee, Y. Ikushima, M. Arai, Adv. Synth. Catal. 346 (2004) 661–668.
[39] C.Y. Xi, H.Y. Cheng, J.M. Hao, S.X. Cai, F.Y. Zhao, J. Mol. Catal. A: Chem. 282 (2008) 80–84.
[40] B.M. Bhanage, Y. Ikushima, M. Shirai, M. Arai, Chem. Commun. (1999) 1277–1278.
[41] S. Fujita, S. Akihara, M. Arai, J. Mol. Catal. A: Chem. 249 (2006) 223–229.
[42] H.W. Lin, C.H. Yen, C.S. Tan, Green Chem. 14 (2012) 682–687.
[43] M. Jorge, M. Natalia, D.S. Cordeiro, J. Phys. Chem. C 111 (2007) 17612–17626.
[44] G. Moakes, J. Janata, Acc. Chem. Res. 40 (2007) 720–728.
[45] P. Politzer, J.S. Murray, M.C. Concha, J. Phys. Org. Chem. 21 (2008) 155–162.
[46] L.W. Diamond, N.N. Akinfiev, Fluid Phase Equilib. 208 (2003) 265–290.
[47] M. Jorge, M. Cordeiro, J. Phys. Chem. C 111 (2007) 17612–17626.
[48] Y.S. Jung, R.A. Marcus, J. Am. Chem. Soc. 129 (2007) 5492–5502.
[49] C. Roosen, M. Ansorge-Schumacher, T. Mang, W. Leitner, L. Greiner, Green Chem. 9 (2007) 455–458.
[50] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of Xps Data, Perkin-Elmer, Physical Electronics Division, Eden Prairie, 1992.
[51] Y.F. Hao, R.X. Liu, X.C. Meng, H.Y. Cheng, F.Y. Zhao, J. Mol. Catal. A: Chem. 335 (2011) 183–188.