Green Route for the Preparation of *p*-Aminophenol from Nitrobenzene by Catalytic Hydrogenation in Pressurized CO₂/H₂O System

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Supporting Information

ABSTRACT: The preparation of *p*-aminophenol from nitrobenzene by one-pot catalytic hydrogenation and *in situ* acidcatalyzed Bamberger rearrangement was first realized in a pressurized CO_2/H_2O system. By employing Pt–Sn/Al₂O₃ as catalyst, nitrobenzene could be converted to *p*-aminophenol with selectivity as high as 85% when the reaction was carried out at 140 °C under 5.5 MPa CO_2 and 0.2 MPa H_2 . This new protocol is environmentally benign because it is fully rid of the use of mineral acid by the application of self-neutralizable carbonic acid.

INTRODUCTION

p-Aminophenol (PAP) is a significant intermediate in the synthesis of pharmaceuticals, pesticides, dyestuffs, and photographic chemicals.¹ PAP can be prepared from *p*-nitrophenol using Fe/HCl as reducing agents, but in the process, a large amount of Fe/FeO sludge (1.2 kg/kg of product) is generated.² PAP can also be prepared by hydrogenation of nitrobenzene (NB) to N-phenylhydroxylamine (PHA) combined with PHA's Bamberger rearrangement³ in the presence of acid,⁴ and this route has been industrialized by Mallinckrodt Inc. (U.S.A.)⁵ with aniline (AN) produced by PHA's further hydrogenation as the main byproduct. For the hydrogenation of NB to PHA in this reaction, various supported noble catalysts⁶ have been reported, even Au supported on TiO₂ has recently been proved to be capable of catalyzing the reaction with a PAP's selectivity of 81%.7 Among the above-mentioned catalysts, Pt catalysts are considered as the best for the selective formation of PAP.⁸ Usually sulfuric acid is used for the rearrangement of PHA to PAP in this reaction. However, it not only causes corrosion of the reactor but also inevitably needs a neutralization step to separate PAP from the reaction mixture during which a large volume of effluents is generated. Therefore, several alternative methods have been tried to eliminate the above-mentioned problem. Chaudhari et al.⁹ used ion-exchange resins to replace sulfuric acid to obtain PAP from NB using Pt-S/C catalyst, but the selectivity of PAP was only 14%. Komatsu et al.¹⁰ introduced Pt supported on H-ZSM-5 to carry out the hydrogenation of NB to PAP and obtained PAP with a selectivity of 66%. $Pt-S_2O_8^{2-}/ZrO_2^{11}$ and Pb-Pt/MgAPO-5¹² have also been prepared and applied by Zhao's group in the hydrogenation of NB to PAP, and the selectivity turned out to be 46.6% and 71%, respectively. Simple mechanical mixture of Pt supported on MgLa mixed oxide¹³ with ZrSAD-3 solid acid has been tested by Abhay et al.¹⁴ for the hydrogenation of NB to PAP, and the selectivity has been claimed to be 94%. All the above-mentioned works applied a common strategy to use solid acid to promote the rearrangement of PHA to PAP, but coke formation¹⁰ occurring on the acid sites of the catalyst will restrict the catalysts' performance and lifetime.

It is known that carbonic acid formed in pressurized CO_2/H_2O system is an attractive environmental benign alternative to conventional permanent mineral acid, and the system has been applied in various reactions such as hydrolysis,¹⁵ dehydration,¹⁶ diazotization,¹⁷ and reductions.¹⁸ In our previous studies, the reduction of nitroarenes to the corresponding aromatic amines by iron proceeded successfully in this system with high yield and high chemoselectivity.¹⁹ Also, the preparation of *N*-arylhydroxylamines by the partial reduction of nitroarenes using zinc under 0.1 MPa CO₂ has been successfully accomplished with the yield from 88% to 99%.²⁰ Furthermore, the Bamberger rearrangement of PHA was also realized in CO₂/H₂O system with a PAP's selectivity of 80%.²¹ Thus, it is significant to make further efforts to investigate the hydrogenation of NB to PAP in the system. In this paper, the preparation of PAP from NB by catalytic hydrogenation in pressurized CO_2/H_2O system is demonstrated.

RESULTS AND DISCUSSION

Effect of Different Catalysts on the Hydrogenation of NB to PAP. From the results shown in Table 1, it can be seen that the Ni or Co catalyst is not good for the formation of PAP (entries 17 and 18). When Ru catalyst is applied, the selectivity of PAP is only 13% (entry 16). The selectivity of PAP is found to be promising when Pt or Pd catalysts are used (entries 1, 4, 7, 10, and 12).

To further improve the selectivity of PAP, the dimethyl sulfoxide (DMSO), which has been reported as an effective additive in terms of enhancing PAP's selectivity of the reaction,^{22,23} is added into the system. From the results shown in entries 2, 5, 11, and 13, it is observed that the addition of DMSO leads to the increase of PAP's selectivity by 10-15%, but it also results in the decrease of NB's conversion because of its toxic effect on the catalysts.²²

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Table 1. Effect of Different Catalysts for the Hydrogenation of NB to PAP^a

				products ^c [%]			
entry	catalyst (metal loading: wt %)	$n_{ m NB}/n_{b}$ metal	conv. of NB ^c [%]	PAP	AN	sel. of PAP [%	
1	Pt/C(Pt:5%)	10000	37	17	20	46	
2^d	Pt/C(Pt:5%)	10000	25	14	11	56	
3	Pt-Pb/C(Pt:5%)	10000	28	16	12	57	
4	Pt/SiO ₂ (Pt:2%)	10000	37	16	21	43	
5 ^d	Pt/SiO ₂ (Pt:2%)	10000	26	15	11	56	
6	Pt-Pb/SiO ₂ (Pt:2%)	10000	20	12	8	61	
7	Pt/Al ₂ O ₃ (Pt:0.5%)	10000	35	18	17	51	
8	Pt-Sn/ Al ₂ O ₃ (Pt:0.5%)	10000	27	16	11	59	
9	Pt-Sn/ Al ₂ O ₃ (Pt:0.04%)	10000	26	18	8	69	
10	Pd/C(Pd:2%)	10000	58	22	36	38	
11^d	Pd/C(Pd:2%)	10000	48	25	23	53	
12	Pd/C(Pd:5%)	10000	57	19	38	34	
13 ^d	Pd/C(Pd:5%)	10000	50	25	25	49	
14	$Pd-CaCO_3-PbO/$ $PbAc_2$ (Pd:5%)	10000	37	23	14	62	
15 ^e	Pd-BaSO ₄ - Quinoline (Pd:5%)	10000	41	24	17	59	
16	Ru/C(Ru:5%)	10000	90	12	78	13	
17	Raney Ni(Ni:≥90%)	10	14	1	13	7	
18	Raney Co(Co: > 99%)	10	11	1	10	9	

^{*a*}Reaction condition: NB = 10 mmol, $H_2O = 60$ mL, $P_{CO_2} = 5.0$ MPa (initial pressure at room temperature), $P_{H_2} = 0.2$ MPa, T = 140 °C, stir rate = 1000 r/min, t = 3 h. ^{*b*}Molar ratio of NB and metal. ^{*c*}Determined by HPLC. ^{*d*}Dimethyl sulfoxide 1.0 mg. ^{*e*}Quinoline 0.05 mL.

The addition of DMSO is effective on enhancing the selectivity of PAP, but it may create problems in the subsequent product isolation. Therefore, Pb or Sn, which has been reported as an effective metal modifier to influence the catalyst's performance in selective hydrogenation reactions,²⁴ is applied. The results show that the selectivity when the reaction is catalyzed by modified Pd or Pt catalysts (entries 3, 6, 8, 9, 14, and 15) can be 10-28%higher than those by monometallic catalysts (entries 1, 4, 7, and 12).

Among the catalysts examined in Table 1, $Pt-Sn/Al_2O_3$ catalyst, which is also effective for the hydrogenation of ketones,²⁵ aldehydes,²⁶ and N-alkylation of amines, exhibits to be the best for the selective formation of PAP,²⁷ with AN and a small amount of *o*-aminophenol (OAP, the concentration ratio of PAP to OAP is around 15–20 in the reaction mixture according to quantitative analysis by HPLC) as byproducts.

Hydrogenation of NB under Different CO₂ Pressure. Because the Bamberger rearrangement of the intermediate PHA to PAP is acid-catalyzed and CO₂ pressure is an important factor to determine the acidity of the CO₂/H₂O system, different CO₂ pressures were applied for the hydrogenation of NB to PAP by using two kinds of catalysts: Pt–Pb/SiO₂ and Pt–Sn/Al₂O₃, with results presented in Figure 1A and Figure 1B, respectively. Without CO₂ in the system, there is hardly any PAP produced by employing Pt–Pb/SiO₂ as catalyst, indicating that carbonic acid is essential for PAP's formation (Figure 1A). By using Pt–Sn/Al₂O₃ as catalyst, a PAP selectivity of 47% is obtained due to the support Al₂O₃'s acidity (Figure 1B). With the increase of initial CO₂ pressure from 0 to 3 MPa, the pH value of the system



Figure 1. Hydrogenation of NB under different CO₂ pressure by using Pt–Pb/SiO₂ catalyst. Reaction condition: NB = 5 mmol, Pt–Pb/SiO₂ (Pt: 0.04%; molar ratio of Pb and Pt: 3; 2 µmol Pt), H₂O 50 = mL, P_{H_2} = 0.5 MPa, T = 140 °C, stir rate = 1000 r/min, t = 4 h, P_{CO_2} : initial pressure at room temperature. Hydrogenation of NB under different CO₂ pressure by using Pt–Sn/Al₂O₃ catalyst. Reaction condition: NB 5 mmol, Pt–Sn/Al₂O₃ (Pt: 0.04%; molar ratio of Sn and Pt: 3; 2 µmol Pt), H₂O 50 mL, P_{H_2} = 0.5 MPa, T = 140 °C, stir rate = 1000 r/min, t = 4 h, P_{CO_2} : initial pressure at room temperature.

decreases from 3.9 to 3.5 as reported,²⁸ and the selectivity by using Pt–Pb/SiO₂ and Pt–Sn/Al₂O₃ catalyst increase gradually to 56% and 65%, respectively. However, when the initial CO₂ pressure is higher than 3 MPa, the pH value does not change as rapidly and apparently as it does when the CO₂ pressure is around 0–3 MPa, therefore, the selectivity of PAP hardly increases. These results are just correlated with the relationship between the CO₂ pressure and the acidity of the system which we previously studied,²⁸ and also in accordance with the fact that stronger acidity favors the rearrangement of PHA to PAP.

Effect of Hydrogenation Temperature on the Formation of PAP. The reaction was studied within a range of temperatures from 100 to 160 °C. It is observed from Figure 2 that higher reaction temperature favors the formation of PAP; the selectivity of PAP increases from 50% to 65% while the temperature changes from 100 to 160 °C. There are two factors accounting for the results. First, the increase of reaction temperature favors PHA's desorption from the catalyst surface to acidic aqueous phase where it undergoes an acid-catalyzed rearrangement process away from further hydrogenation. Second, the rearrangement of PHA to PAP catalyzed by a weaker acid should be conducted at a relatively high temperature to obtain a high selectivity of PAP, which is already verified by Wei et al.; they have investigated the rearrangement of PHA catalyzed by three different kinds of acids: H2SO4, HCl, and H_3PO_4 ²⁹ Their research shows that when the temperature is lower than 60 °C, the selectivity of PAP in the catalytic reaction



Figure 2. Effect of hydrogenation temperature on the formation of PAP. Reaction condition: NB = 5 mmol, Pt–Sn/Al₂O₃ (Pt:0.04%; molar ratio of Sn and Pt: 3; 2 μ mol Pt), H₂O = 50 mL, P_{CO2} = 5.5 MPa (at reaction temperature, 3 MPa initially at room temperature), P_{H2} = 0.5 MPa, stir rate = 1000 r/min, *t* = 4 h.

using strong acid H_2SO_4 (or HCl) is higher than that using the moderate strong acid H_3PO_4 . However, if the catalytic reaction is carried out under a temperature of 90 °C, the selectivity of PAP using H_3PO_4 is the best.

Reaction Results with Different nNB/nPt (Molar Ratio of NB to Pt). Keeping the other reaction conditions constant, the catalytic hydrogenation of NB with different $n_{\text{NB}}/n_{\text{Pt}}$ was examined. From the results presented in Figure 3, it can be seen



Figure 3. Reaction results with different $n_{\text{NB}}/n_{\text{Pt}}$. Reaction condition: Pt-Sn/Al₂O₃ (Pt: 0.04%; molar ratio of Sn and Pt: 3; 2 µmol Pt), H₂O = 50 mL, P_{CO_2} = 5.5 MPa (at reaction temperature, 3 MPa initially at room temperature), P_{H_2} = 0.5 MPa, T = 140 °C, stir rate = 1000 r/min, t = 4 h.

that the selectivity of PAP increases from 65% to 80% with the increase of $n_{\rm NB}/n_{\rm Pt}$ from 2500 to 12500. More NB's competitive adsorption on the catalyst surface might favor the intermediate PHA's desorption into the aqueous phase to rearrange into PAP, afterward leading to more PAP produced.

Hydrogenation of NB under Different H₂ **Pressure.** The results in Figure 4 show that both the conversion of NB and the yields of PAP and AN increase with the increase of H₂ pressure, but the selectivity of PAP declines gradually. It is known that the increase of H₂ pressure will lead to the increase of the hydrogenation rate. With the increase of H₂ pressure, the formation rate of PHA, which will convert to PAP or AN, increases; therefore, both the yield of PAP and the yield of AN increase. However, PHA's desorption rate from the catalyst is constant with the temperature maintained at 140 °C, and the generated PHA, which cannot desorb from the catalyst in time



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Figure 4. Hydrogenation of NB under different H₂ pressure. Reaction conditions: NB = 20 mmol, Pt-Sn/Al₂O₃ (Pt: 0.04%; molar ratio of Sn and Pt: 3; 2 μ mol Pt), H₂O = 50 mL, P_{CO2} = 5.5 MPa (at reaction temperature, 3 MPa initially at room temperature), *T* = 140 °C, stir rate = 1000 r/min, *t* = 4 h.

are further hydrogenated to give more AN, leading to the decline of PAP's selectivity.

Hydrogenation of NB at Different Stir Rates. Because the hydrogenation of NB to PAP is a complex four-phase heterogeneous reaction including gas, solid catalyst, aqueous, and organic phases,³⁰ the change of reaction parameters which can accelerate the diffusion and enhance the mass transfer will benefit the formation of PHA, and those which can facilitate PHA's desorption from catalyst and efficient transport to acidic phase will enhance PAP's selectivity. There's no doubt that the increase of stir rate would favor the selectivity of PAP, and it is also observed that the selectivity rises dramatically from 67% to 85% when the stir rate increases from 500 to 1000 rpm in Table 2. The selectivity does not change much when the stir rate is beyond 1000 rpm, so 1000 rpm is chosen for the following studies.

Table (2. H	vdrog	enation	of NB	at]	Different	Stir	Rates
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			produ [%	ucts ^b	
entry	stir rate/(r/min)	conv. of NB ^{b} [%]	PAP	AN	sel. of PAP [%]
1	500	9	6	3	67
2	750	16	13	3	81
3	1000	20	17	3	85
4	1250	20	17	3	85
^a Dooct	ion condition. M	B = 20 mmal Dt	Sm / 11	<u>о</u> (т	0+.0 01%, malar

"Reaction condition: NB = 20 mmol, Pt–Sn/Al₂O₃ (Pt:0.04%; molar ratio of Sn and Pt: 3; 2 μ mol Pt), H₂O = 50 mL, P_{H₂} = 0.2 MPa, P_{CO₂} = 5.5 MPa (at reaction temperature, 3 MPa initially at room temperature), *T* = 140 °C, *t* = 4 h. ^bDetermined by HPLC.

Results of NB's Hydrogenation with Different Reaction Time. Figure 5 shows that the conversion of NB and the yields of PAP and AN increase with the prolongation of reaction time, but the selectivity of PAP gradually decrease. With the consumption of substrate NB, there would be lower $n_{\rm NB}/n_{\rm Pt}$ along with lower selectivity of PAP. These results are consistent with the results in Figure 3. After the NB has been consumed for 6 h, the nNB/nPt of the system is nearly 7500, and the selectivity of PAP turns out to be about 70% in Figure 5. Besides, with the reaction time prolonging, the color of the reaction liquid changes gradually from pale yellow to dark brown, as a result of the generated PAP's conversion into other byproducts³¹ such as 4, 4'-diaminodiphenyl ether (detectable in the reaction liquid when the reaction



Figure 5. Results of NB's hydrogenation with different reaction time. Reaction condition: NB = 20 mmol, Pt–Sn/Al₂O₃ (Pt: 0.04%; molar ratio of Sn and Pt: 3; 2 μ mol Pt), H₂O = 50 mL, P_{CO2} = 5.5 MPa (at reaction temperature, 3 MPa initially at room temperature), P_{H2} = 0.2 MPa, *T* = 140 °C, stir rate = 1000 r/min.

time is longer than 6 h). The byproduct may be another cause of PAP selectivity's decrease.

Reusability of the Catalyst. In order to test the reusability of the catalyst, the used $Pt-Sn/Al_2O_3$ was collected by centrifugation, washed with methanol, dried in vacuum atmosphere at 120 °C, and then recharged to the reactor for the next run. NB was added according to the weight of the reused catalyst to keep the initial $n_{\rm NB}/n_{\rm Pt}$ constant. The results in Figure 6 indicate that the conversion of NB decreases by 4%, and the



Figure 6. Reusability study of the catalyst. Reaction condition: $n_{\rm NB}/n_{\rm Pt} = 10\,000$, Pt–Sn/Al₂O₃ (Pt: 0.04%; molar ratio of Sn and Pt: 3; 2 μ mol Pt), H₂O = 50 mL, $P_{\rm H_2} = 0.2$ MPa, $P_{\rm CO_2} = 5.5$ MPa (at reaction temperature, 3 MPa initially at room temperature), T = 140 °C, stir rate = 1000 r/min, t = 4 h.

selectivity of PAP decreases by 7% after 4 runs, which may be caused by the adsorbed species³² on the catalyst's surface. The catalyst shows a total turnover number of 5400 mol PAP/mol Pt after 4 successive runs.

CONCLUSION

In conclusion, the preparation of *p*-aminophenol from nitrobenzene by catalytic hydrogenation has been realized in a pressurized CO_2/H_2O system. Among the catalysts examined in Table 1, Pt–Sn/Al₂O₃ catalyst exhibits to be the best for the selective formation of PAP. PAP's selectivity of 85% is obtained when the reaction is carried out at 140 °C under 5.5 MPa CO_2 and 0.2 MPa H_2 by employing Pt–Sn/Al₂O₃ catalyst. The

catalyst shows a total turnover number of 5400 mol PAP/mol Pt after 4 successive runs.

EXPERIMENTAL SECTION

Materials and Reaction Procedure. $Pt-Sn/Al_2O_3$ catalysts were donated by Dalian institute of chemical physics, Chinese academy of sciences and prepared by the vacuum complex impregnation method.³² Pt-Pb/C (5%) and Pt-Pb/SiO₂ (5%) catalysts were prepared as follows: Carbon black (Vulcan XC-72, 2 g) or silica (Aerosil 300, 2 g) was impregnated with an aqueous solution of H_2PtCl_6 (0.5 mmol Pt) and $(CH_3COO)_2Pb$ (1.5 mmol Pb) for 24 h, dried at 120 °C, calcined at 500 °C for 4 h and finally reduced in hydrogen atmosphere at 300 °C for 3 h. The other catalysts and all the chemicals were purchased from commercial sources.

A 100 mL autoclave (Parr 4842) was applied to carry out the reaction of NB to PAP. The nitrobenzene, catalyst, and water were introduced into the autoclave which was then purged three times with 0.2 MPa CO_2 . Then CO_2 was gradually charged into the autoclave to maintain a designated pressure. H₂ was charged when the autoclave reached the designated temperature under constant stirring. The total operating pressure was maintained constant by continuous recruitment of H₂ during the reaction process. After the reaction, the gas was released slowly. The suspension was filtered, the solid was washed with methanol, and then the filtrate was dissolved in methanol in order to obtain a 250 mL homogeneous solution. The above solution was diluted for 10 times and quantitatively analyzed by high-performance liquid chromatography.

Product Analysis. The analytical method used was similar to that reported.¹² Agilent 1100 series high-performance liquid chromatography (HPLC) instrument equipped with a UV detector was used with the following conditions: Mobile phase (vacuum filtered before use): (A) 70 mmol/L aqueous solution of ammonium acetate; (B) methanol. Gradient: $t = 0 \min 70\%$ A 30% B, $t = 20 \min 0\%$ A 100% B; flow rate: 1.0 mL/min; column: Agilent TC-C18 column, 5 μ m, 4.6 mm × 250 mm; column temperature: 30 °C; UV detector: 254 nm.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.5b00307.

The HPLC method used in product analysis was described in detail (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) (a) Osborne, C. Paracetamol: A Curriculum Resource; Royal Society of Chemistry: Cambridge, 2002. (b) Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed.; Seidel, A., Ed.; Wiley Interscience: New York, 1992, Vol. 2; pp 481–580.

(2) Rode, C. V.; Vaidya, M. J.; Chaudhari, R. V. Org. Process Res. Dev. **1999**, 3, 465–470.

(3) Bamberger, E. Ber. Dtsch. Chem. Ges. 1894, 27, 1548-1557.

(4) (a) Henke, C. O.; Vaughen, J. V. Reduction of aryl nitro compounds. U.S. Patent 2,198,249, 1940. (b) March, J. Advanced Organic Chemistry; McGraw-Hill Book Company: New York, 1977.

Organic Process Research & Development

(5) Caskey, D. C. ; Chapman, D. W. Process for preparing *p*-aminophenol and alkyl substituted *p*-aminophenol. U.S. Patent 4,571,437, 1986.

(6) (a) Rylander, P. N.; Karpenko, I. M.; Pond, G. R. Process for preparing para-aminophenol. U.S. Patent 3,715,397, 1973. (b) Derrenbacker, E. L. Process for the selective preparation of *p*-aminophenol from nitrobenzene. U.S. Patent 4,307,249, 1981. (c) Gao, Y.; Wang, F. D.; Liao, S. J.; Yu, D. R. *React. Kinet. Catal. Lett.* 1998, 64, 351–357. (d) Chandrashekha, V. R.; Manisha, J. V. ; Raghunath, V. C. Single step hydrogenation of nitrobenzene to p-aminophenol. U.S. Patent 6,403,833, 2002.

(7) Zou, L. Y.; Cui, Y. Y.; Dai, W. L. Chin. J. Chem. 2014, 32, 257-262.

(8) Sathe, S. S.; Heights, M. Process for preparing *p*-aminophenol in the presence of dimethyldodecylamine sulphate. U.S. Patent 4,176,138, 1978.

(9) Chaudhari, R. V.; Divekar, S. S.; Vaidya, M. J.; Rode, C. V. Single step process for the preparation of *p*-aminophenol. U.S. Patent 6,028,227, 2000.

(10) Komatsu, T.; Hirose, T. Appl. Catal., A 2004, 276, 95-102.

(11) Wang, S. F.; Ma, Y. H.; Wang, Y. J.; Xue, W.; Zhao, X. Q. J. Chem. Technol. Biotechnol. 2008, 83, 1466–1471.

(12) Wang, S. F.; He, B. B.; Wang, Y. J.; Zhao, X. Q. Catal. Commun. 2012, 24, 109–113.

(13) Kantam, M. L.; Kochkar, H.; Clacens, J. M.; Veldurthy, B.; Garcia-Ruiz, A.; Figueras, F. *Appl. Catal.*, B **2005**, 55, 177–183.

(14) Deshpande, A.; Figueras, F.; Kantam, M. L.; Ratnam, K. J.; Reddy, R. S.; Sekhar, N. S. *J. Catal.* **2010**, *275*, 250–256.

(15) Rayner, C. M. Org. Process Res. Dev. 2007, 11, 121-132.

(16) (a) Hunter, S. E.; Savage, P. E. Ind. Eng. Chem. Res. 2003, 42, 290-

294. (b) Hunter, S. E.; Ehrenberger, C. E.; Savage, P. E. J. Org. Chem. 2006, 71, 6229–6239. (c) Hunter, S. E.; Savage, P. E. AIChE J. 2008, 54, 516–528.

(17) Tundo, P.; Loris, A.; Selva, M. Green Chem. 2007, 9, 777-779.

(18) (a) Li, G. P.; Jiang, H. F.; Li, J. H. Green Chem. 2001, 3, 250–251.

(b) Jiang, H. F.; Huang, X. Z. J. Supercrit. Fluids 2007, 43, 291–294.
(c) Jiang, H. F.; Dong, Y. S. Chin. J. Chem. 2008, 26, 1407–1410.

(19) Gao, G.; Tao, Y.; Jiang, J. Y. Green Chem. 2008, 10, 439–441.

(20) Liu, S. J.; Wang, Y. H.; Jiang, J. Y.; Jin, Z. L. *Green Chem.* **2009**, *11*, 1397–1400.

(21) (a) Liu, S. J.; Hao, Y. P.; Jiang, J. Y. *Ind. Eng. Chem. Res.* **2014**, *53*, 8372–8375. (b) Jiang, J. Y.; Liu, S. J.; Hao, Y. P. Process for preparing *p*-aminophenol from N-phenylhydroxylamine in pressurized CO_2/H_2O system. CN Patent 102,001,954, 2011.

(22) Rylander, P. N.; Karpenko, I. M.; Pond, G. R. Ann. N. Y. Acad. Sci. **1970**, 172, 266–275.

(23) Min, K. I.; Choi, J. S.; Chung, Y. M.; Ahn, W. S.; Ryoo, R.; Lim, P. K. *Appl. Catal.*, A **2008**, 337, 97–104.

(24) (a) Adúriz, H. R.; Gígola, C. E.; Sica, A. M.; Volpe, M. A.; Touroude, R. *Catal. Today* 1992, 15, 459–467. (b) Didillon, B.; Candy, J. P.; Le Peletier, F.; Ferretti, O. A.; Basset, J. M. *Stud. Surf. Sci. Catal.* 1993, 78, 147–154. (c) Coq, B.; Tijani, A.; Figuéras, F. J. *Mol. Catal.* 1992, 71, 317–333. (d) Anderson, J. A.; Mellor, J.; Wells, R. P. K. J. *Catal.* 2009, 261, 208–216. (e) Yin, M. Y.; He, S. B.; Yu, Z. K.; Wu, K. K.; Wang, L. D.; Sun, C. L. *Chin. J. Catal.* 2013, 34, 1534–1542.

(25) Torres, G. C.; Ledesma, S. D.; Jablonski, E. L.; de Miguel, S. R.; Scelza, O. A. *Catal. Today* **1999**, *48*, 65–72.

(26) (a) Serrano-Ruiz, J. C.; Huber, G. W.; Sánchez-Castillo, M. A.; Dumesic, J. A.; Rodríguez-Reinoso, F.; Sepúlveda Escribano, A. J. Catal.
2006, 241, 378–388. (b) Zgolicz, P. D.; Rodríguez, V. I.; Vilella, I. M. J.; de Miguel, S. R.; Scelza, O. A. Appl. Catal., A 2011, 392, 208–217.
(c) He, S. B.; Sun, C. L.; Du, H. Z.; Dai, X. H.; Wang, B. Chem. Eng. J.
2008, 141, 284–289.

(27) He, W.; He, S. B.; Sun, C. L.; Wu, K. K.; Wang, L. D.; Yu, Z. K. *Cuihua Xuebao* **2012**, *33*, 717–722.

(28) Gao, G.; Jiang, J. Y. Comput. Appl. Chem. 2011, 28, 359-362.

(29) Wei, S. P.; Qin, G. H.; Wei, Z. M.; Weng, D. H. Huaxue Shijie 2003, 9, 482-484.

(30) Rode, C. V.; Vaidya, M. J.; Jaganathan, R.; Chaudhari, R. V. *Chem. Eng. Sci.* **2001**, *56*, 1299–1304. (31) Sun, G. Q. Master Thesis, Qingdao University of Science and Technology, Qingdao, China, 2008.

(32) He, S. B.; Sun, C. L.; Bai, Z. W.; Dai, X. H.; Wang, B. Appl. Catal., A 2009, 356, 88–98.