Electronic Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information

Precipitation of chitosan from ionic liquid solutions by compressed CO_2 anti-solvent method

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Experimental Section

Materials: Chitosan with a stated deacetylation degree of 80.0-95.0% and viscosity of 50-800 mPa·S was purchased from Sinopharm Chem. Reagent Co. Ltd, and dried at 150 °C under vacuum before dissolution. N_2 (99.999%) and CO_2 (99.995%) were purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd. (Beijing, China). The IL [Bmim]OAc used in the experiment, which with a purity over 99.9 wt% was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). The water contents of IL was determined by Karl-Fischer titration (Karl Fisher ZDJ-400S, Multifunctional titrator, Beijing Xianqu Weifeng Company, Beijing, China) after drying it at 45 °C under vacuum conditions for 96 h, and it has a water content less than 1000 ppm. All chemicals in the Strecker reactions were purchased from Sinopharm Chem. Reagent Co. Ltd. Analytical thin layer chromatography (TLC) was carried out using Merck 0.2 mm silica gel 60 F-254 aluminum sheets.

Determination of chitosan solubility in [Bmim]OAc: The dried [Bmim]OAc (about 5.0 g) was added in a 100 ml, 3-neck, round-bottom flask. The flask was then immersed in an oil bath (DF-101S, Henan Yuhua Instrument Factory). The temperature instability of the oil bath was estimated to be ±1.0 °C. Under the continuous stirring, finely grinding chitosan powder (0.1 wt% of the IL) was added into the flask. Starting at 40 °C, this mixture was heated and stirred under a certain atmosphere (air, nitrogen, or carbon dioxide). Additional chitosan (another 0.1 wt% of the IL) was added until the solution became clear, and we viewed the chitosan was saturated in the IL when the chitosan could not be dissolved under the certain temperature within 2 h. For each situation, the temperature was increased by 10 °C, up to the maximum temperature of 140 °C.

Verification of the existence of acetic acid in [Bmim]OAc above 140 °C**:** The samples of [Bmim]OAc were prepared. Under the continuous stirring, each of them was heated for 10 h at different temperatures from 40 °C to 140 °C with 10 °C intervals. Attenuated Total Reflection Fourier Transform Infra Red (ATR-FTIR) Spectroscopy was then implemented to investigate the produce of acetic acid. The experiments were carried out at a Prestige-21 FTIR spectrometer (Shimadzu, Japan) using a single reflection ATR cell. Acquisition was accomplished in the DTGS detector mode using an accumulation rate of 40 scans at a resolution of 4 cm^{-1} at room temperature (~ 25 °C) in the spectral range of 400 to 4600 cm^{-1}. Triplicates of each sample were measured.

Recovery of chitosan from IL by CO_2 antisolvent method: The apparatus consisted of a high-pressure view cell with a variable volume of 20-50 ml, a water bath at constant temperature controlled by a YKKY A2 digital temperature controller with the accuracy ± 0.1 °C, a high-pressure syringe pump (DB-80), a gas cylinder, a magnetic stirrer and a pressure gauge with a accuracy of ± 0.025 MPa in the pressure range of 0-22 MPa. In a typical experiment, 1 g chitosan/[Bmim]OAc solution was loaded into the view cell that was placed in the water bath with the desired temperature. The air was removed and then CO_2 was charged into the cell after the thermal equilibrium had been reached. The system was laid up under a certain temperature and pressure for a period of time and then removed under vacuum to exhaust CO_2. The aerogels was washed completely by deionized water and calculated the isolated yields of regenerated chitosan. For comparison, the chitosan was regenerated from the mixture of chitosan + ILs by addition of ethanol.

Measurement of solvatochromic parameters of [Bmim]OAc/CO_2 mixtures at different pressures: The solvatochromic parameters were determined by the absorption peaks of three dyes, N,N-diethyl-4-nitro-aniline (DENA), 4-nitroaniline (NA) and Reichardt's dye 33. The measurement apparatus consisted of a gas cylinder, a high-pressure UV sample cell, a high-pressure pump, a pressure gauge, and a temperature controller. The optical path length and the inner volume of the cell were 21 mm and 6.5 mL, respectively. Three kinds of stock solution were prepared by adding the dyes in methanol and mixed homogeneously. The methanol was then removed by placing the solutions under vacuum at 40 °C. In a typical experiment, the suitable amount of [Bmim]OAc solution was loaded into the sample cell. Then CO_2 was charged until the desired pressure was reached and a magnetic stirrer was used to enhance the mixing of CO_2 and [Bmim]OAc. After that, the UV-vis absorbance spectrum was recorded by a TU-1201 Model spectrophotometer (Beijing General Instrument Company). The determined wavelengths of three dyes at the maximum absorption were used to calculate the solvatochromic parameters and the λ_{max} stated is the average of three separate scans. According the references 15,

The π^* parameters were determined using DENA, using eqn. (1) and (2)

$$\pi^* = 0.314(27.52 - \nu_{(\mathrm{DENA})}) \qquad (1)$$

$$\nu_{(\mathrm{Dye})} = 1/(\lambda_{(\mathrm{Dye})\mathrm{max}} \times 10^{-4}) \qquad (2)$$

The β values were determined using DENA and NA, using eqn. (3)

$$\beta = (1.035\nu_{(\mathrm{DENA})} + 2.64 - \nu_{(\mathrm{NA})})/2.80 \qquad (3)$$

The α values were determined by the $E_T(30)$ and π*, using eqn. (4), (5) and (6)

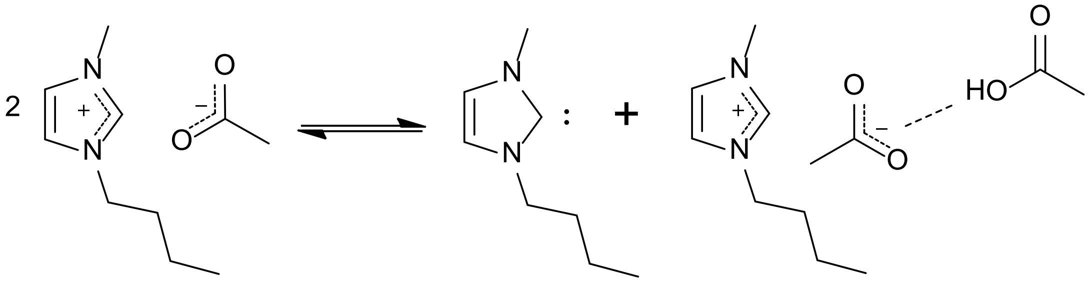
$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \qquad (4)$$

$$E_T(30) = 0.9986E_T(33) - 8.6878 \qquad (5)$$

$$E_T(33) = 28592/\lambda_{(\mathrm{RD33})\mathrm{max}} \qquad (6)$$

Characterization of the regenerated chitosan: FTIR spectra were recorded with KBr pellets on a Prestige-21 FTIR Spectroscopy (Shimadzu, Japan), and a total of 40 scans were taken for each sample at a resolution of 4 cm^{-1}. The crystal phases of the native and regenerated chitosan were identified at room temperature with XRD (Rigaku D/max-2500) using Cu Kα as X-ray radiation under 40 kV and 200 mA. The scanning range is 2θ = 5-60° with a step of 2θ = 0.02° and 0.5 s per step. The TGA curves were determined with a TA Instruments Q50-TG thermal analyser using platinum crucibles. 5-10 mg chitosan was loaded in the platinum crucible, and the measurements were carried out under flowing N_2 at a heating rate of 10 °C min^{-1}. The morphologies of the chitosan materials with different treatment were examined by transmission electron microscopy (TEM; JEOL JEM-2010).

Synthesis of imines catalyzed by chitosan: A mixture of amine (about 1 mmol), aldehyde (about 1 mmol), and a definite store of catalysts (I, II or III) was dissolved in 0.5 ml of ethanol, and then was stirred at room temperature. As indicated by precipitation of solid products from the liquid mixture and by TLC experiments using authentic samples, the reaction can be viewed as completion already. After the crude product was recrystallized from ethanol, the redundant solvent can be removed via vacuum freeze drying treatment and thus to afford pure desired imines. Finally, ^1H NMR (400 MHz) spectra and FT-IR spectra of the imines were obtained to confirm the structure of the imines.



Scheme S1 According the reference 13, the proposed reaction for the imidazolium cation and acetate anion of [Bmim]OAc to form a carbene intermediate and acetic acid via proton transfer above 140 °C.

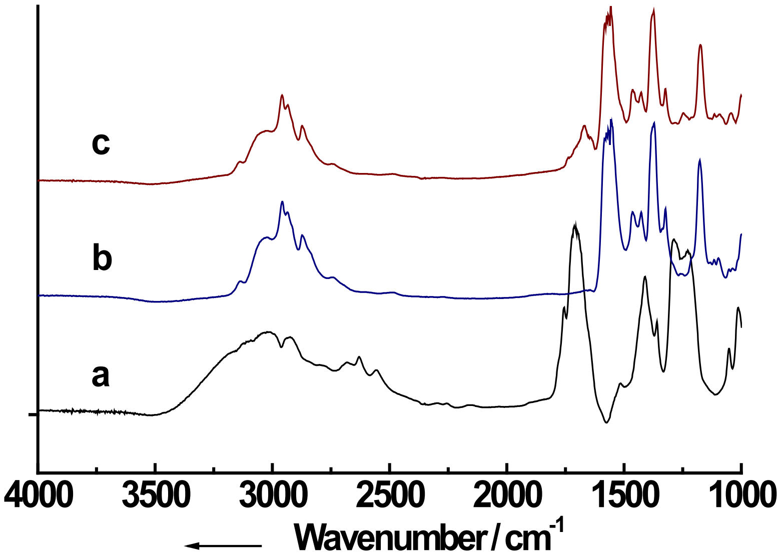


Fig. S1 ATR-FTIR spectra of pure acetic acid (a), pure [Bmim]OAc at 25 °C (b), and [Bmim]OAc at 140 °C (c).

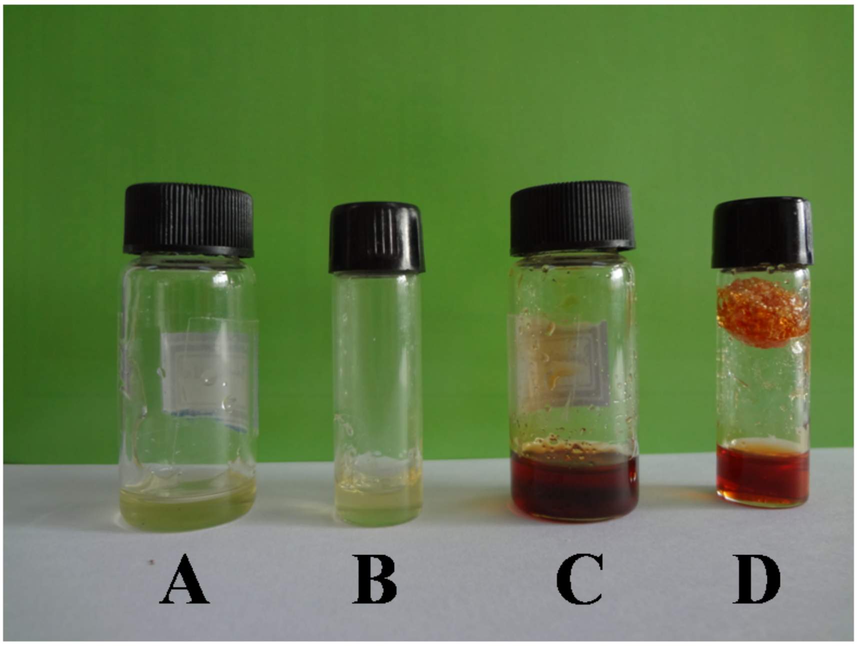


Fig. S2 Photos of 3.0 wt% (A and B) and 6.0 wt% (C and D) chitosan/[Bmim]OA solution with adding compressed CO_2 as anti-solvent (B and D) and without adding compressed CO_2 as anti-solvent (A and C).

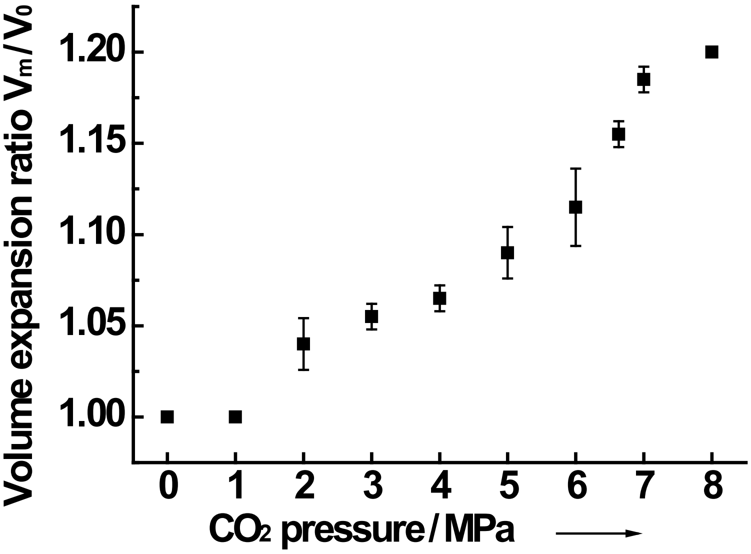


Fig. S3 The volume expansion ratio (V_m/V_0) of 9.0 wt% chitosan/ [Bmim]OAc solution at 25 °C after charging compressed CO_2.

Characterization of the regenerated and native chitosan

The native and regenerated chitosan have been characterized in order to compare their structure. FTIR spectra (Fig. S4) of the native and regenerated chitosan from [Bmim]OAc show that the spectra of four kinds of chitosan materials are quite similar, which indicates that no chemical reaction takes place during the dissolution and recovery processes. In other words, the main chain of chitosan has not been destroyed in both processes after using IL and anti-solvents. As can be vividly seen in the XRD profiles (Fig. S5), the native chitosan shows a better diffraction pattern with two obvious diffraction peaks at $2\theta = 10.7$ and 19.9 degrees than the regenerated chitosan with only one at 19.9 degrees. It suggests that all the regenerated chitosan exhibits worse crystallization degree than the native one. Maybe in the process of dissolving, some inter- and intra-molecular hydrogen bonds were destroyed. As a result, the regenerated chitosan has a more disorder crystalline structure. Particularly, the crystallinity of regenerated chitosan decreased significantly after dissolution in [Bmim]OAc and recovery by compressed CO_2. From the TGA curves (Fig. S6), for the native chitosan, the rapid decomposition occurs near by the temperature of 300 °C, while for the regenerated ones from compressed CO_2, ethanol or deionized water, this temperatures are about 200 °C, and it has a more residual mass after the decomposition step. That is to say, the regenerated sample gives an obviously more char yield on pyrolysis. As has been verified by XRD profiles, some inter- and intra-molecular hydrogen bonds of the native chitosan were destroyed in the dissolving in IL, and it can be also used to explain the TGA curves that some relatively unstable impurities maybe exist in the regenerated samples. From Transmission Electron Microscopy (TEM) (Fig. S7), we can infer that the micro-particles were formed after disposing the regenerated chitosan via compressed CO_2, and exhibited a high surface area comparing the other three samples.

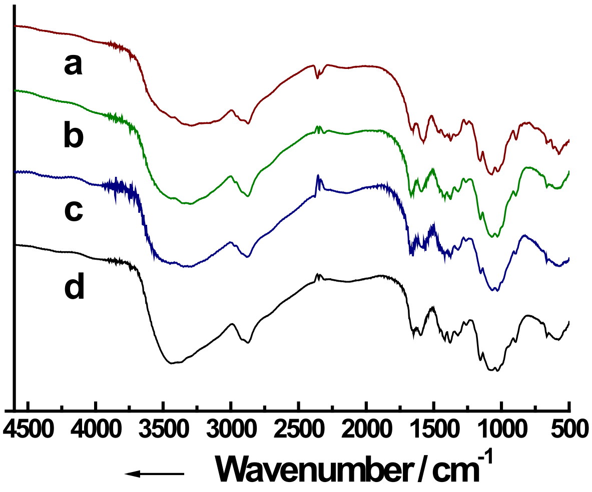


Fig. S4 FTIR spectra of the native and regenerated chitosan, including the chitosan regenerated from [Bmim]OAc/chitosan by addition of compressed CO_2 (a), ethanol (b) and deionized water (c), and the native chitosan (d).

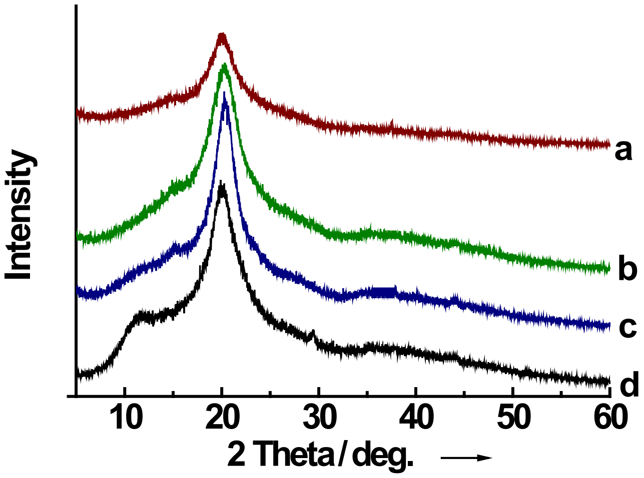


Fig. S5 X-ray diffraction patterns of the native and regenerated chitosan, including the chitosan regenerated from [Bmim]OAc/chitosan by addition of compressed CO_2 (a), ethanol (b), deionized water (c), and the native chitosan (d).

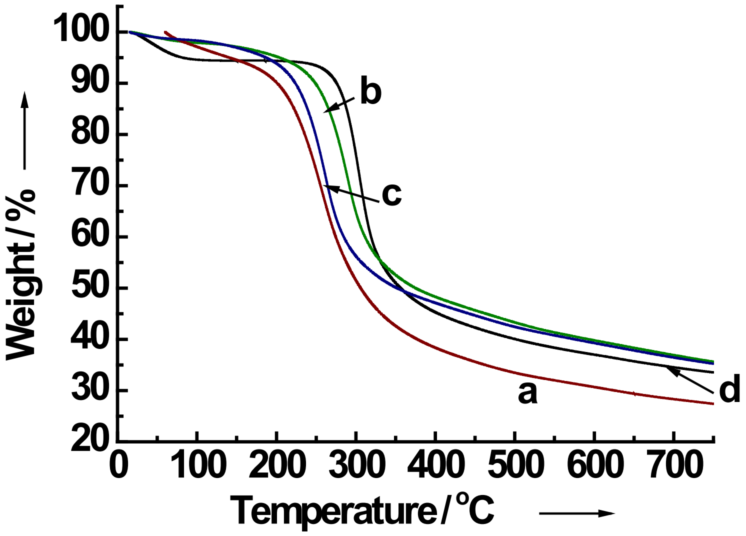


Fig. S6 Thermal decomposition profiles of the native and regenerated chitosan, including the chitosan regenerated from [Bmim]OAc/chitosan by addition of compressed CO_2 (a), ethanol (b), deionized water (c), and the native chitosan (d).

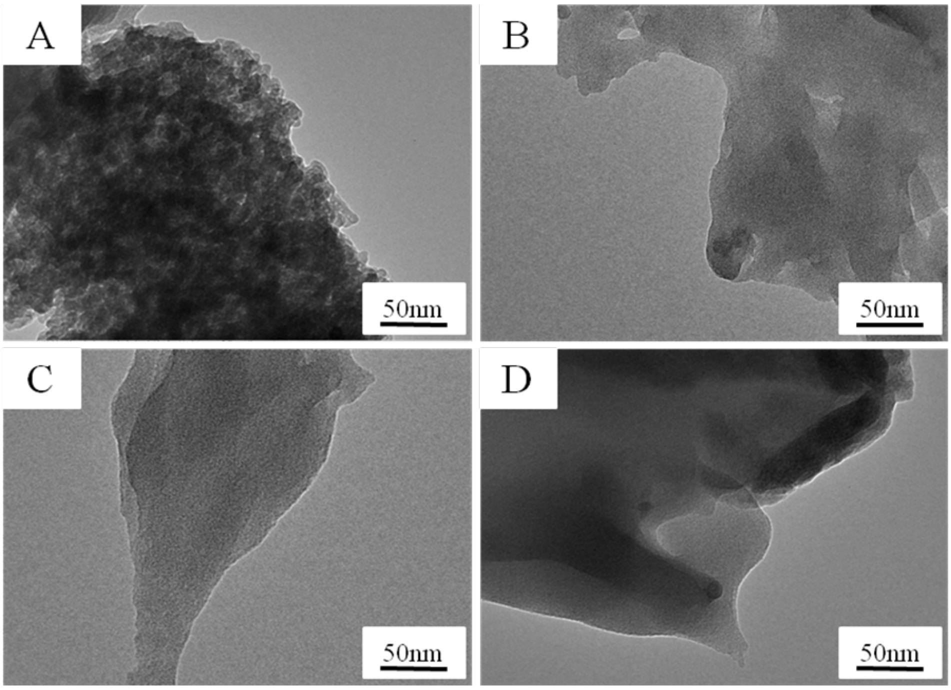
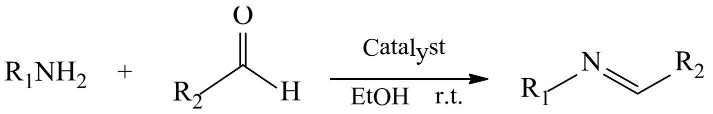


Fig. S7 TEM patterns of the native and regenerated chitosan, including the chitosan regenerated from [Bmim]OAc/chitosan by addition of compressed CO_2 (A), deionized water (B), ethanol (C), and the native chitosan (D).

Table S1 Preparation of imines by the reaction catalyzed by chitosan under mild condition.



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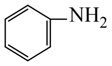
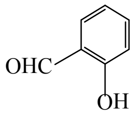
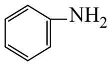
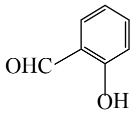
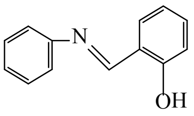
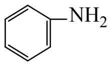
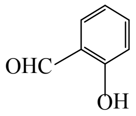
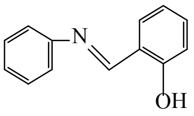
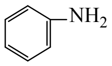
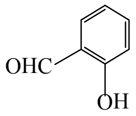
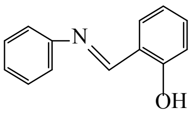
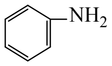
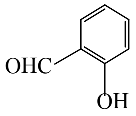
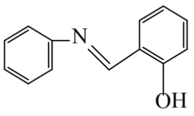
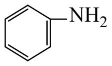
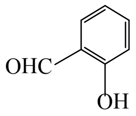
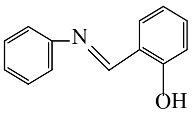
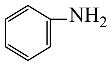
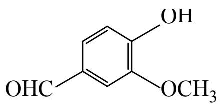
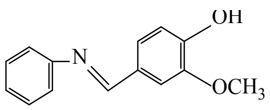
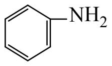
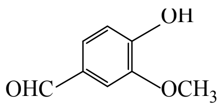
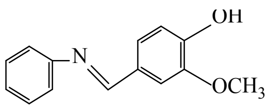
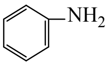
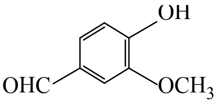
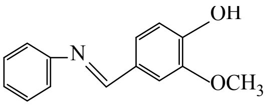
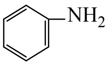
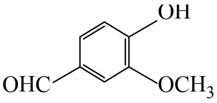
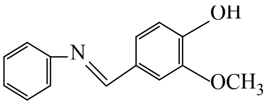
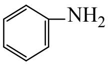
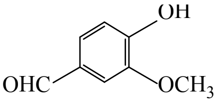
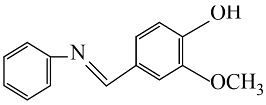
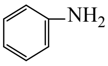
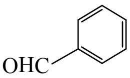
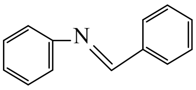
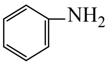
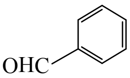
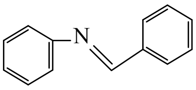
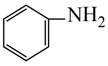
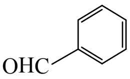
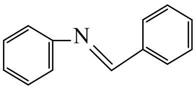
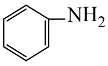
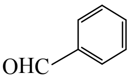
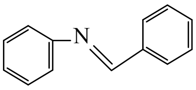
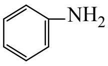
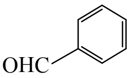
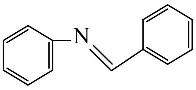
1			--	--	24	--
2			I		6	81
3			I		3	36
4			II		4.5	94
5			II		3	67
6			III		3	96
7			I		12	88
8			I		2	9

9			II		4	99
10			II		2	64
11			III		2	99
12			I		6	85
13			I		3	16
14			II		4	94
15			II		3	73
16			III		3	96

[a] Three kinds of catalysts: I) the native chitosan; II) the regenerated chitosan by ethanol; III) the regenerated chitosan by compressed CO_2 were used in the experiment. [b] Isolated yields.