Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.911116

55 (2015) 70–76
June

Taylor & Francis
Taylor & Francis Group

Removal of urea from wastewater by heterogeneous catalysis

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Received 12 November 2013; Accepted 30 March 2014

ABSTRACT

In order to find an effective method for urea removal from wastewater, a number of experiments were conducted in a batch reactor with α-Al_2O_3 and η-Al_2O_3 as catalysts, respectively. The results indicate that η-Al_2O_3 catalyst shows significantly higher urea removal rate than α-Al_2O_3 catalyst or the thermal hydrolysis, and the removal rate increases with increasing temperature, catalyst dosage and reaction time. Using η-Al_2O_3 catalyst, the urea concentration in wastewater is reduced to less than 1 mg/L at 165℃ after 150 min. The reaction kinetics study shows that the hydrolysis of urea behaves as a pseudo-first-order reaction. From the calculated rate constants, η-Al_2O_3 exhibits an excellent catalytic activity for urea hydrolysis, whereas the activity of α-Al_2O_3 is considerably weak. In addition, the η-Al_2O_3 catalyst possesses good recycling ability. The slight loss of activity of η-Al_2O_3 should be attributed to the generation of a small amount of hydrated aluminas, and the activity can be recovered by calcination.

Keywords: Urea removal; Wastewater; Catalyst; Reaction kinetics; Stability

1. Introduction

Urea is the most widely used nitrogen fertilizer in agriculture on a global scale, and it is produced in excess of 140 million tons per year worldwide (http://worldcommoditytraders.com/urea-fertilizers). For every ton of urea produced, 0.3 tons of water is formed based on the synthesis reaction equation, and approximately 0.2 tons of water is introduced into the synthesis process. This means, in a urea plant with a daily output of 1,300 tons urea, about 650 tons of wastewater has to be discharged from the process per day. This wastewater stream usually contains about 0.5–2 wt % urea [1], which is considered deleterious in natural waterways in that it promotes algae growth and hydrolyses slowly, releasing ammonia that is toxic to fish [2,3]. Since the early 70s, due in part to stricter environmental legislation, it has become increasingly necessary to reduce the urea content of plant wastewater. Today's requirements mostly call for a maximum concentration of 10 mg/L [3,4].

There are some methods reported for treating urea wastewater, such as biological [5,6], enzymatic [7] and electrochemical methods [8,9], those are still under investigation and currently have some drawbacks which hinder the industrialization. Thermal hydrolysis process, as a common treatment method in present urea plants, is carried out at an elevated temperature and pressure (200℃, 2 MPa) [3]. A large amount of medium pressure steam is supplied to heat the wastewater fed into hydrolyser, and thus this process is costly and consumes high energy.

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Since catalyst has the ability to accelerate reaction rate, catalytic hydrolysis may be a good method for the removal of urea. However, there is very little information available about catalytic hydrolysis of urea in wastewater in the published literatures. Schell [10] reported a method for hydrolyzing urea in wastewater streams in the presence of vanadium compounds in a semibatch reactor. The 58 and 100% urea conversion could be achieved, when the reaction was, respectively, continued for 360 and 840 min. This treatment process requires too much time, and the vanadium catalysts are toxic and difficult to recycle.

Sahu et al. [11,12] studied the catalytic hydrolysis of urea in aqueous solution of high concentration (10–30 wt %) to produce ammonia with the help of fly ash and α-Al_2O_3 (specific surface area: $0.7388\,m^2/g$). However, the activities of these catalysts are not very satisfactory in this reaction system, and the performances of these catalysts are still unknown for the treatment of wastewater containing low concentration of urea.

Apparently, there is an urgent need to develop a catalyst with high activity and stability for the hydrolysis of urea in wastewater. To avoid secondary pollution and catalyst loss, the use of insoluble solid catalyst probably is a good choice. Therefore, on the basis of thermal hydrolysis, it was decided to deeply study the removal of urea from wastewater in a batch reactor by using η-Al_2O_3 as catalyst in contrast with α-Al_2O_3 and thermal hydrolysis (no catalyst). The effects of temperature, catalyst dosage and reaction time on the removal rate of urea were investigated, and the reaction kinetics and catalyst performance were studied.

2. Experimental

2.1. Materials

Diacetyl monoxime ($C_4H_7NO_2$, ≥98.0%) and thiosemicarbazide (CH_5N_3S, ≥98.5%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Urea ($CO(NH_2)_2$, ≥99.0%), phosphoric acid (H_3PO_4, ≥85.0%) and sulphuric acid (H_2SO_4, ≥98.0%) were from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). All materials were of analytical grade and used without further purification. Diacetyl monoxime, thiosemicarbazide, phosphoric acid and sulphuric acid were used for determination of urea in solution.

η-Al_2O_3 (Jiezhong, Zibo, China) was of industrial grade to be used as catalyst to catalyze the hydrolysis of urea, which was calcined for activation at a temperature of 550℃ for 4 h. α-Al_2O_3 was prepared by calcining the η-Al_2O_3 at 1,200℃ for 4 h. Before the experiment, the two aluminas were crushed to 150–200 mesh powder for use.

2.2. Characterization

X-ray diffractograms were recorded with Shimadzu (Japan) XRD-6000 diffractometer equipped with Cu Kα anode ($\lambda = 0.15405$ nm). The specific surface areas of catalysts were measured by a multipoint BET method using nitrogen adsorption at −196℃ on an automatic surface analyser (F-sorb 3400, Gold APP Instrument, China).

2.3. Reaction scheme

The hydrolysis of urea to ammonia and carbon dioxide is endothermic, and the overall reaction formula is as follows (Eq. (1)):

$$NH_2CONH_2 + H_2O \xrightarrow{+Heat} 2NH_3 + CO_2 \tag{1}$$

This process employs two reaction steps (Eqs. (2) and (3)) [4,13]:

$$\begin{aligned} &NH_2CONH_2(l) + H_2O(l) \xrightarrow{-Heat} NH_2COO^- + NH_4^+ \\ &\quad \Delta H_{298} = -23\text{kJ/mol} \end{aligned} \tag{2}$$

$$\begin{aligned} &NH_2COO^- + NH_4^+ \xrightarrow{+Heat} 2NH_3(l) + CO_2(l) \\ &\quad \Delta H_{298} = +84\text{kJ/mol} \end{aligned} \tag{3}$$

It is apparent that completion of the reactions is favoured by high temperature. Eq. (2), in which urea is hydrolyzed to form ammonium carbamate, is a mildly exothermic and slow reaction, while Eq. (3), which is strongly endothermic, is very fast and goes towards completion [14].

2.4. Experiment method

Solution with a urea concentration of 8.0 g/L was used to simulate industrial urea wastewater. A mixture of 10 mL of the urea solution and a certain quantity of catalyst was placed in a 20 mL Teflon lined reactor, and heated with high-speed stirring at different temperatures (125, 135, 145, 155 and 165℃) and time periods (30, 60, 90, 120 and 150 min). After the reaction, the mixture was rapidly cooled to room temperature and filtered. The filtrate was analysed by the diacetyl monoxime colorimetric method [15] to determine the urea concentration remaining in the aqueous solution, and the separated catalyst was washed with distilled water and dried at 110℃ for 12 h for reuse. The removal rate of urea was calculated using the following Eq. (4):

$$\text{Removal rate}\,(\%) = \frac{C_0 - C_A}{C_0} \times 100 \tag{4}$$

where C_0 is the initial concentration of urea and C_A is the final urea concentration after reaction.

3. Results and discussion

3.1. XRD characterization of catalysts

Fig. 1 depicts XRD patterns of α-Al_2O_3 and η-Al_2O_3. The XRD pattern of α-Al_2O_3 catalyst shows evident diffraction peaks at 25.6°, 35.2°, 43.4° and 57.5°. Judging from the high and sharp diffraction peaks, the sample shows a high degree of crystallinity. The crystal structure of α-Al_2O_3 is hexagonal close packed that consists of close-packed planes of oxygen and aluminium [16]. This means that its chemical activity should be relatively low. The η-Al_2O_3 powder exhibits obvious diffraction peaks at 37.4°, 39.7°, 46.0° and 66.8°, and it has a spinel-cubic structure with a regular cubic-oxygen lattice [17]. It is known that η-Al_2O_3 has a large specific surface area, and is commonly used as a heterogeneous catalyst and often exhibits high catalytic activity.

3.2. Effect of temperature

Experiments were conducted at different temperatures and the results have been shown in Fig. 2. The removal rate increases sharply from 5.61 to 76.6% in the process of thermal hydrolysis. On addition of catalysts, the trend remains the same as the graph without catalyst, and the removal rate increases from 15.4 to 96.0% for η-Al_2O_3. The above results indicate that the hydrolysis temperature is an important parameter, which may be due to that the overall reaction is endothermic. Furthermore, η-Al_2O_3 shows obviously higher removal rate of urea than α-Al_2O_3, which may be attributed to the fact that the specific surface area of η-Al_2O_3 (194.0 m^2/g) is larger than that of α-Al_2O_3 (1.489 m^2/g), so η-Al_2O_3 catalyst can provide more active sites.

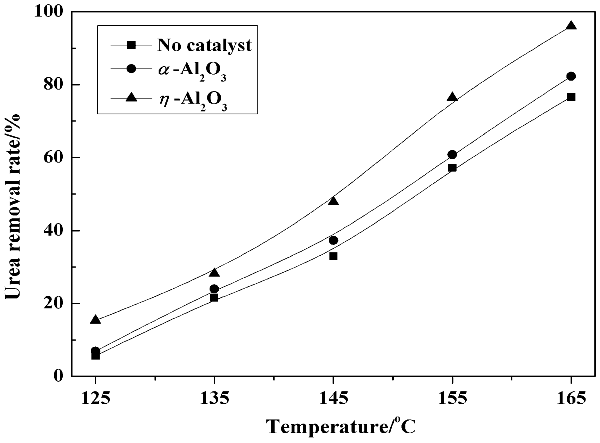

Fig. 2. Effect of temperature on urea removal rate (catalyst dosage: 50 g/L; reaction time: 60 min).

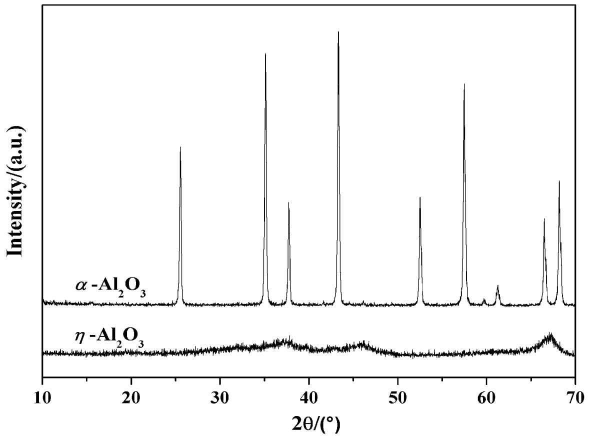

Fig. 1. XRD patterns of α-Al_2O_3 and η-Al_2O_3.

3.3. Effect of reaction time

The effect of reaction time on urea removal rate has been shown in Fig. 3. Initially, the urea removal rate in the presence of η-Al_2O_3 as catalyst is obviously higher than no catalyst or α-Al_2O_3 and increases steeply with increasing reaction time. Beyond 120 min, the difference among the three curves is slight, but can be

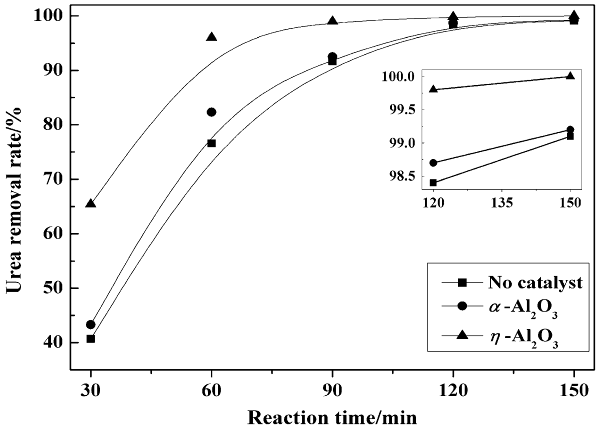

Fig. 3. Effect of reaction time on urea removal rate (catalyst dosage: 50 g/L; temperature: 165℃).

easily distinguished in the enlarged figure. Without catalyst and with α-Al_2O_3 catalyst, the urea concentrations in the liquid residue are still as high as 74.82 and 68.95 mg/L after 150 min, respectively, which cannot meet the discharge requirement for urea wastewater (10 mg/L). It is worth mentioning that, using η-Al_2O_3 catalyst, the concentration of urea is reduced to less than 1 mg/L for the same reaction time. From the above results, it can be concluded that η-Al_2O_3 catalyst is able to significantly promote urea hydrolysis to reach the completion due to its high catalytic activity.

3.4. Effect of catalyst dosage

Fig. 4 shows the effect of the η-Al_2O_3 dosage on urea removal rate. Initially, the urea removal rate increases rapidly with increasing η-Al_2O_3 dosage. This trend should be because the number of active sites increases as the dosage of η-Al_2O_3 increases, and thus urea hydrolysis reaction can be catalyzed by more active sites. But beyond the certain value of 50 g/L, the removal rate reaches almost a constant value, which should be mainly due to the high resistance of liquid membrane; at this time, external diffusion may become an important factor influencing the heterogeneous catalysis reaction.

3.5. Reaction kinetics

It is necessary to investigate the kinetics for the further study of catalytic performance of η-Al_2O_3. Excluding mass transfer limitations, a series of experiments on urea hydrolysis were conducted at a constant η-Al_2O_3 dosage of 50 g/L, and at different temperatures and reaction times. It can be seen from Fig. 5(a) that the urea concentration in the liquid residue decreases as reaction time increases at a fixed temperature, and the higher temperature possesses less concentration of urea than low temperature.

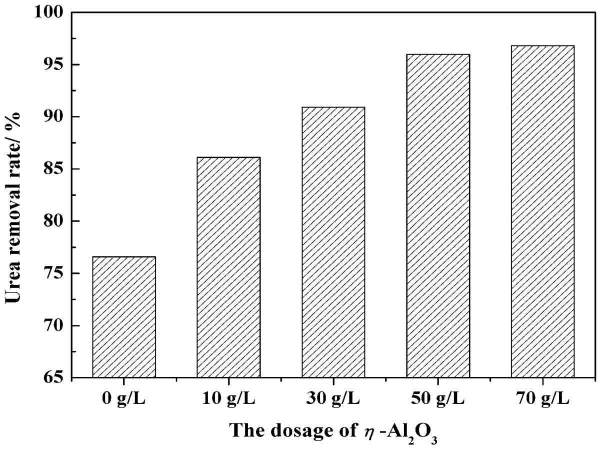

Fig. 4. Effect of the η-Al_2O_3 dosage on urea removal rate (temperature: 165℃; reaction time: 60 min).

Assuming no backward reaction, the rate for forward reaction can be written as (Eq. (5)):

$$-\frac{dC_A}{dt} = k\,(C_A)^n \tag{5}$$

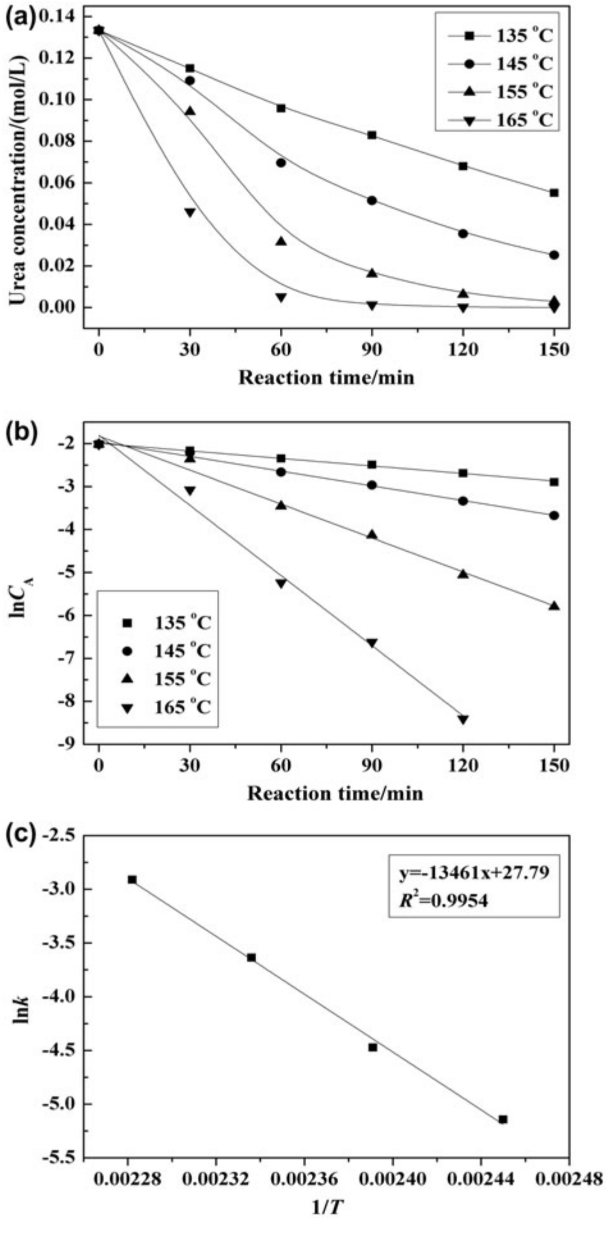

Fig. 5. (a) Effect of reaction time on urea concentration with η-Al_2O_3 as catalyst at different temperatures. (b) Plot of t vs. $\ln C_A$ with η-Al_2O_3 as catalyst at different temperatures. (c) Plot of $1/T$ vs. $\ln k$ with the η-Al_2O_3 as catalyst.

where k is the forward rate constant, t is the reaction time, and n is the reaction order. Since water in the urea solution is in excess, the concentration of water can be neglected. To calculate the rate constant in the presence of η-Al_2O_3 as catalyst, the pseudo-first-order kinetic model was presumed. The kinetic equation of pseudo-first-order model is as follows (Eq. (6)):

$$\ln C_A = \ln C_0 - kt \tag{6}$$

Fig. 5(b) shows the plots of t vs. $\ln C_A$ with η-Al_2O_3 as catalyst at different temperatures, and the values of k are calculated and noted in Table 1. As seen from Table 1, the high correlation coefficients ($R^2 > 0.987$) obtained confirm that the catalytic hydrolysis of urea in the presence of η-Al_2O_3 could well follow the pseudo-first-order kinetic model. The value of rate constant is found to increase rapidly from 5.840×10^{-3} to $5.443 \times 10^{-2}\,\text{min}^{-1}$ for an increase in reaction temperature from 135 to 165℃.

The graph of $1/T$ vs. $\ln k$ with η-Al_2O_3 as catalyst is shown in Fig. 5(c). According to the Arrhenius theory, the pre-exponential factor (A) and activation energy (E_a) were, respectively, calculated as $1.172 \times 10^{12}\,\text{min}^{-1}$ and $111.9\,\text{kJ/mol}$.

In the same method, the kinetics studies without catalyst and with α-Al_2O_3 (50 g/L) as catalyst were, respectively, conducted. Fig. 6(a) and (b) depicts the effect of reaction time on urea concentration. From the concentration time data, the rate constant, pre-exponential factor and activation energy were calculated and listed in Tables 2a and 2b, respectively, for the two cases. Whether without catalyst or with α-Al_2O_3 catalyst, as same as η-Al_2O_3, the order of urea hydrolysis is close to one, and the rate constant increases with increasing temperature.

The value of k at any temperature can be calculated by the Arrhenius equation, and the graphs of temperature vs. rate constant (135–165℃) are shown in Fig. 7. It can be seen that the rate constant with α-Al_2O_3 catalyst is slightly higher than no catalyst. That is, α-Al_2O_3 has the catalytic activity for urea hydrolysis, but the activity is considerably weak. It is readily apparent that the rate constant with η-Al_2O_3 as catalyst is significantly higher than no catalyst or α-Al_2O_3, and the difference of rate constants increases rapidly with increasing temperature, which indicates that η-Al_2O_3 shows an excellent catalytic activity for the hydrolysis of urea in low concentration.

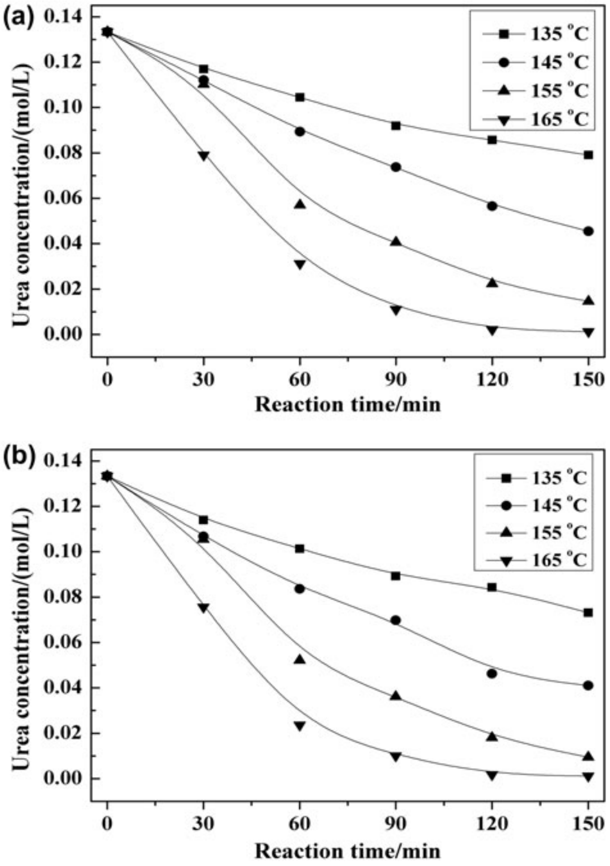

Fig. 6. (a) Effect of reaction time on urea concentration without catalyst at different temperatures. (b) Effect of reaction time on urea concentration in the presence of α-Al_2O_3 catalyst at different temperatures.

Table 1
Kinetics data for urea hydrolysis with η-Al_2O_3 as catalyst[a]

Temperature/℃	Pseudo-first-order model			
	Kinetics equation	R^2	n	$k \times 10^3/(\text{min}^{-1})$
135	$\ln C_A = -1.995-0.005840t$	0.9950	1	5.840
145	$\ln C_A = -1.957-0.01142t$	0.9930		11.42
155	$\ln C_A = -1.827-0.02636t$	0.9872		26.36
165	$\ln C_A = -1.805-0.05443t$	0.9893		54.43

[a]The dosage of η-Al_2O_3 is 50 g/L.

Table 2a
Kinetics data for urea hydrolysis without catalyst

	Pseudo-first-order model				
Temperature/℃	$k \times 10^3$/(min^{-1})	R^2	n	A/(min^{-1})	E_a/(kJ/mol)
135	3.500	0.9840	1	8.017×10^{11}	112.3
145	7.260	0.9960			
155	15.41	0.9837			
165	33.82	0.9722			

Table 2b
Kinetics data for urea hydrolysis in the presence of α-Al_2O_3 as catalyst[a]

	Pseudo-first-order model				
Temperature/℃	$k \times 10^3$/(min^{-1})	R^2	n	A/(min^{-1})	E_a/(kJ/mol)
135	3.840	0.9840	1	3.981×10^{11}	109.6
145	8.010	0.9915			
155	17.97	0.9804			
165	34.18	0.9733			

3.6. Stability test

An important evaluating standard for the heterogeneous catalyst is its ability for reuse and recovery. The results of reused η-Al_2O_3 catalysts are shown in Table 3. It is found that urea concentration in the liquid residue slowly increases with the increase of reused times, that is the catalytic activity of η-Al_2O_3 slightly decreases as the reused times increase (the third reused catalyst shows the lowest catalytic activity). However, the urea concentration remained less than 7 mg/L, when the catalyst was reused for the third time, and thus the η-Al_2O_3 catalyst shows good recycling ability. When the catalyst after the third reuse was calcined at 550℃ for 4 h, the catalytic activity of the catalyst can be recovered (fourth reused catalyst).

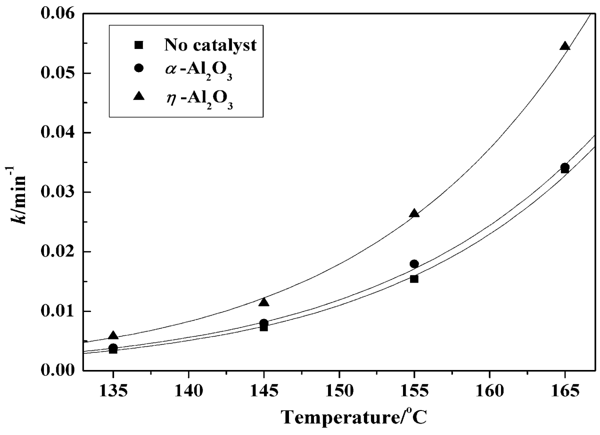

Fig. 7. Graphs of temperature vs. rate constant.

The XRD patterns of η-Al_2O_3 catalyst before and after reaction are presented in Fig. 8. For the third reused catalyst (curve b), a series of weak diffraction peaks of hydrated aluminas were observed besides the main peaks of η-Al_2O_3, but these diffraction peaks of hydrated aluminas disappeared completely for the fourth reused catalyst (curve c). Therefore, the slight loss of activity could be due to the generation of hydrated aluminas ($Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3$; $Al_2O_3 + H_2O \rightarrow 2AlOOH$) on the surface of the

Table 3
Recycling of catalyst used in the removal of urea[a]

Catalyst	Urea removal rate %	Urea concentration in the liquid residue (mg/L)
Fresh catalyst	>99.9	<1
1st reused catalyst	>99.9	1.13
2nd reused catalyst	>99.9	5.01
3rd reused catalyst	>99.9	6.36
4th reused catalyst[b]	>99.9	2.20

[a] Reaction condition: temperature: 165℃; catalyst dosage: 50 g/L; and reaction time: 150 min.

[b] Before reuse, the catalyst sample was calcined at 550℃ for 4 h.

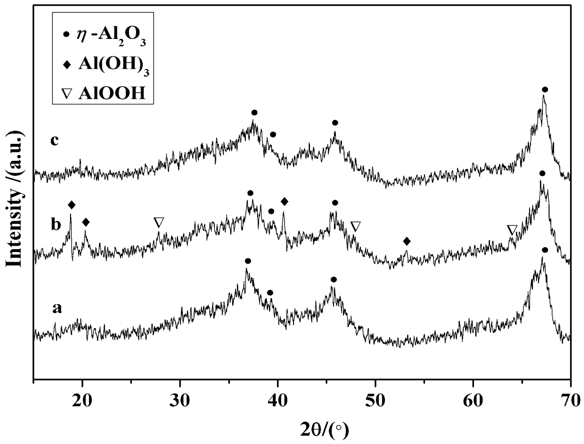

Fig. 8. XRD patterns of η-Al_2O_3 catalyst before and after reaction ((a) fresh catalyst; (b) third reused catalyst; (c) fourth reused catalyst).

catalyst, and the catalytic activity can be recovered by calcination can be attributed to the transformation from hydrated alumina to alumina.

4. Conclusions

Heterogeneous catalytic hydrolysis of urea is a potential alternative technique to simple thermal hydrolysis for the treatment of urea wastewater. It is found from the experiment that urea removal rate increases with increasing temperature, catalyst dosage and reaction time, and η-Al_2O_3 exhibits higher urea removal rate than the thermal hydrolysis or α-Al_2O_3. On addition of η-Al_2O_3 catalyst, the effect of urea hydrolysis is greatly promoted, and the urea concentration is decreased to less than 1 mg/L at 165℃ after 150 min. The reaction kinetics study indicates that urea hydrolysis is a pseudo-first-order reaction. With η-Al_2O_3 as catalyst, the rate constant increases rapidly with temperature, from 5.840×10^{-3} at 135 to $5.443 \times 10^{-2}\,\text{min}^{-1}$ at 165℃, and the pre-exponential factor and activation energy were, respectively, found to be $1.172 \times 10^{12}\,\text{min}^{-1}$ and 111.9 kJ/mol. η-Al_2O_3 shows excellent catalytic activity and recycling ability for urea hydrolysis. The slight loss of activity of η-Al_2O_3 should be attributed to the generation of hydrated aluminas, and the activity can be recovered by calcination. Moreover, α-Al_2O_3 has a certain catalytic activity for the hydrolysis of urea in wastewater, but the activity is considerably weak.

Acknowledgement

The authors are grateful to the Shanxi science and technology key project (project number: 2012032 1003-02).

List of symbols

A	—	frequency factor, min^{-1}
C_A	—	final urea concentration after reaction, mol/L
C_0	—	initial concentration of urea, mol/L
E_a	—	activation energy, kJ/mol
ΔH	—	change in enthalpy, kJ/mol
k	—	forward rate constant, min^{-1}
n	—	order of the forward reaction, dimensionless
R^2	—	correlation coefficient, dimensionless
T	—	temperature, K
t	—	time, min

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