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HNCO hydrolysis performance in urea-water solution thermohydrolysis process with and without catalysts*

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Abstract: The thermolysis of urea-water solution and its product, HNCO hydrolysis is investigated in a dual-reactor system. For the thermal decomposition below about 1073 K, the main products are ammonia (NH_3) and isocyanic acid (HNCO) whereas at higher temperatures the oxidation processes take effect and the products include a low concentration of nitric oxide (NO) and nitrous oxide (N_2O). The gas HNCO is quite stable and a high yield of HNCO is observed. The ratio of NH_3 to HNCO increases from approximately 1.2 to 1.7 with the temperature. The chemical analysis shows that H radical is in favor of HNCO hydrolysis by instigating the reaction $HNCO+H\cdot \rightarrow \cdot NH_2+CO$ and high temperature has positive effect on H radical. The hydrolysis of HNCO over an alumina catalyst made using a sol-gel process (designated as γ-Al_2O_3) is investigated. The conversion of HNCO is high even at the high space velocities (6×10^5 h^{-1}) and low temperatures (393–673 K) in the tests with catalysts, which enhances HNCO hydrolysis and raises the ratio of NH_3 to HNCO to approximately 100. The pure γ-Al_2O_3 shows a better catalytic performance than CuO/γ-Al_2O_3. The addition of CuO not only reduces the surface area but also decreases the Lewis acid sites which are recognized to have a positive effect on the catalytic activity. The apparent activation energy of the hydrolysis reaction amounts to about 25 kJ/mol in 393–473 K while 13 kJ/mol over 473 K. The overall hydrolysis reaction rate on catalysts is mainly determined by external and internal mass-transfer limitations.

Key words: Urea-water solution, Sol-gel method, γ-Al_2O_3, HNCO hydrolysis
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1 Introduction

Nitrogen oxides (NO_x) are gaseous pollutants which are primarily formed through a combustion process. Many techniques have been developed to handle NO_x emissions to meet strict regulatory requirements. Due to low operation costs, no influence on initial combustion and easy retrofit alone or in combination with other NO_x control techniques, the selective non-catalytic reduction (SNCR) has been recognized as one of the most cost-efficient techniques for NO_x control. The SNCR process is based on the NO reduction reaction with an amine within a specific temperature range. The most commonly used reagents are ammonia and urea. Ammonia can be obtained as anhydrous liquid or aqueous solution, but in either case the safety issues are quite severe. Ammonia is very toxic to most life forms and highly volatile. Numerous regulations are applied to the safe transport, storage and handing of ammonia. Due to its safety storage and handling process, urea has been widely applied in SNCR processes (Hossain *et al.*, 2005). Urea is decomposed to ammonia (NH_3) and isocyanic acid (HNCO) which are real reagents reacting with NO (Koebel *et al.*, 1996). HNCO can hydrolyze with water, yielding ammonia and carbon dioxide:

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$$NH_2CONH_2 \rightarrow NH_3+HNCO, \tag{1}$$

$$HNCO+H_2O \rightarrow NH_3+CO_2. \tag{2}$$

The hydrolysis reaction (2) is exothermic by −95.9 kJ/mol on stand conditions and its Gibbs free energy is strongly negative, so that the equilibrium lies completely on the right side (Koebel and Strutz, 2003). HNCO is quite stable in the gas phase even under humid conditions, but the hydrolysis easily occurs in many different single and mixed metal oxides (Piazzesi, 2006).

The simplified reaction mechanisms of the SNCR process with ammonia and urea are depicted in Fig. 1. In a urea-based SNCR process, after the thermolysis of urea to HNCO according to reaction (1), HNCO reacts primarily with H radical and OH radical (Miller and Bowman, 1991):

$$HNCO+H\cdot \rightarrow \cdot NH_2+CO, \tag{3}$$

$$HNCO+\cdot OH \rightarrow \cdot NCO+H_2O. \tag{4}$$

The NH_2 radical formed in reaction (3) takes part in the NO removing reactions and the NCO radical undergoes subsequent reaction with NO to form N_2O:

$$\cdot NCO+NO \rightarrow N_2O+CO. \tag{5}$$

The N_2O formed in reaction (5) mainly decomposes in the presence of a third body or reacts with OH radical and H radical to form N_2:

$$N_2O+M \rightarrow N_2+O+M, \tag{6}$$

$$N_2O+\cdot OH \rightarrow N_2+ H_2O, \tag{7}$$

$$N_2O+H\cdot \rightarrow N_2+\cdot OH. \tag{8}$$

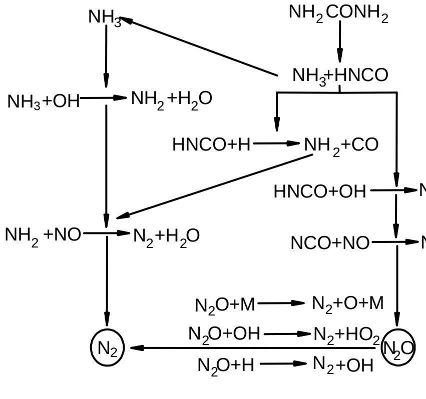

Fig. 1 Major paths for selective non-catalytic reduction

Consequently N_2O and CO are undesirable by-products because they are also air pollutants. Jodal *et al.* (1991) reported that at a lower temperature nitrogen presenting as N_2O was approximately 50% of the reduced NO_x using urea as reductants whereas it was about 20% at the optimum temperature of 1273 K. Muzio and Quartucy (1997) also confirmed that typically 7%–25% of the reduced NO_x was emitted as N_2O whereas it was less than 4% for NH_3.

Many measurements are proposed to eliminate the N_2O emission of urea-SNCR, such as higher reaction temperature, longer resident time (Tayyeb Javed *et al.*, 2007), the use of microwave-plasma discharge (Wójtowicz *et al.*, 2000), and the use of additives (Bae *et al.*, 2006). Recently, KrÖcher and Elsener (2009) proposed converting urea upstream to pure ammonia to avoid the formation of N_2O, CO, or other side-products. They investigated about 20 materials and found γ-Al_2O_3 was the best suited as a fluidized bed material due to its high catalytic activity as well as relatively good stability. It is very difficult for HNCO to convert to NH_3 during urea decomposition and HNCO hydrolysis with a catalyst is a good choice. In the present work, focusing on the NH_3 generation and HNCO's hydrolysis, urea solution pyrolysis with and without a catalyst in a dual-reactor system has been researched to discover the urea and HNCO hydrolysis characteristics in order to find a good method by which to generate ammonia from urea for selective catalytic reduction (SCR) and SNCR/SCR hybrid technology based urea.

2 Experiments

2.1 Catalysts preparation

Spherical γ-Al_2O_3 granular catalysts were prepared by sol-gel process described in (Buelna and Lin, 2004). First, 2 mol/L stable boehmite sols aluminum were synthesized from hydrolysis and condensation of aluminum isopropoxide using the modified Yoldas process (Yoldas, 1975; Buelna and Lin, 2001). Stable boehmite sol was mixed with nitric acid at a predetermined concentration, heated at 343–348 K, and stirred until the mixture became so viscous that it could not be stirred even with the magnetic stirrer driven under maximum power. Second, after aging for half an hour at 343 K, the boehmite reached the gelation point and was dropped in an ammonia solution (10% (v/v) NH_3). The structure of the wet-gel particles was strengthened after aging in the ammonia solution for 1 h. The gel particles were then collected and dried in air at 313 K for 48 h and calcined in air at 823 K for 6 h.

Spherical $CuO/\gamma\text{-}Al_2O_3$ granules containing CuO were prepared by the same method and stable boehmite sol was mixed with copper nitrate solutions instead of nitric acid at a predetermined concentration according to the required loading. The precursor of the active species $Cu(NO_3)_2$ was coated on the surface of the boehmite primary particles and converted to CuO during the calcinations. Elemental analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) confirmed that the mass fraction of CuO in $CuO/\gamma\text{-}Al_2O_3$ granules was 4.57%.

2.2 Catalyst measurement

The Brunauer-Emmett-Teller (BET) surface area, pore volume, and average pore diameter of the catalysts were measured by nitrogen adsorption porosimetry (AWTOSOB, Quantachrome). An X-ray diffractometer (D/max 2550PC, Rigaku) was used to identify the phase structure of the catalysts. An ammonia temperature-programmed desorption (NH_3-TPD) experiment was undertaken by gas chromatography. 100 mg of catalysts were used and the flow rate of He balance gas was 1.8 L/h. TPD experiments were performed by saturating the sample at 393 K with pure NH_3. Before saturation at 393 K, the sample was treated in situ at 723 K for 1 h in flowing He gas to remove water vapor and impurities. After adsorption weakly bound species were desorbed by purging the sample with He. TPD was completed by increasing the temperature up to 723 K at a rate of 11 K/min.

2.3 Experimental methods

For the simultaneous thermolysis and catalytic hydrolysis study, a dual-reactor system shown in Fig. 2 was applied. The experimental apparatus were consisted of an injection system, a reactor system, and an analysis system. The carrying gases, N_2 and O_2, were supplied by gas bottles and mixed in the desired ratios controlled by mass flow controllers prior to the reaction zone. The urea-water solution was pumped by a variable speed peristaltic pump and transported to the gas stream through a stainless steel injector with an internal diameter (ID) of 0.32 mm. To enhance mixing, a bypass nitrogen was mixed with the vapor of the aqueous urea to increase the momentum, then intersected with the carrying gases at the centerline of the reactor. The liquid flow rates were controlled by adjusting the revolutions per minute (RPM) of the pump in accordance with the calibration curve for the pump. The reactors were made of quartz to minimize any catalytic surface reactions. The horizontal reactor (ID of 10 mm) was for urea thermal decomposition. Then, the mainly thermal decomposition products, NH_3 and HNCO, directly flowed into the vertical reactor (ID of 6 mm) packed with or without catalysts. At the exit of the vertical reactor, the gases were analyzed with a Fourier transform infrared (FTIR) spectrometer (Gasmet DX4000, Calcmet software) equipped with a heated multiple pass gas cell (path length=5 m, volume=400 ml and T=180 °C). The instrument was calibrated for the analyses of NH_3, H_2O, N_2O, NO, NO_2, and HNCO with 2% precision.

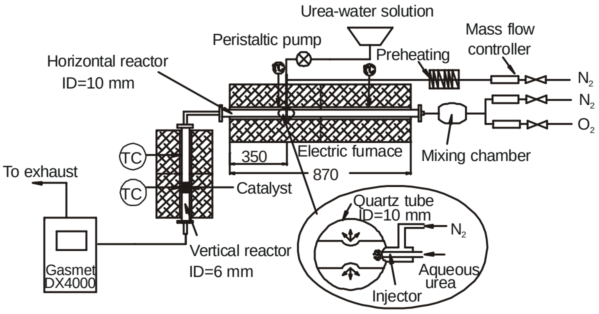

Fig. 2 Schematic of the experimental apparatus

The experiments were conducted with a constant mass flow of 1 L/min. The residence time in the horizontal reactor varied with temperature and was between 0.35 s (at 1273 K) and 0.55 s (at 823 K). A urea-water solution with 21.7 g of urea per liter of water was used and the feed rate of the solution was 0.052 ml/min to keep the volume fraction of water vapor 6% and the urea volume fraction 400×10^{-6}. The urea-water liquid flow rate was changed by adjusting the RPM of the pump and the concentration of urea-water liquid was also altered to ensure the required water vapor concentration and urea volume fraction 400×10^{-6}. About 0.1 ml of catalysts were filled in a fixed bed reactor at 393–673 K and the particle size of catalysts were 150–250 μm, which minimized the effect of pressure drop and mass transfer. The overall gas flow rate was 1 L/min which meant the gas hourly space velocity (GHSV) amounted to 6×10^5 h^{-1}.

3 Results and discussion

3.1 Catalysts characteristics

The X-ray diffraction (XRD) patterns of the catalysts are shown in Fig. 3. The patterns for the samples with peaks at about 2θ=37°, 47° and 67° were typical of γ-Al_2O_3. The speciality peaks of pure CuO appeared at 2θ=35.5° and 38.7°. No peaks of copper oxide were detected though the ICP-AES confirms 4.57% CuO in the CuO/γ-Al_2O_3. The absence of peaks corresponding to CuO in CuO/γ-Al_2O_3 indicated that the active species were coated on the surface of the support in a monolayer or submonolayer form (Friedman *et al.*, 1978; Strohmeier *et al.*, 1985). Also the results showed that the XRD spectrums of the catalysts indicated no obvious difference between the fresh and used. The bulk phase was not changed after 20-h usage, indicating that the catalysts have a good structural stability.

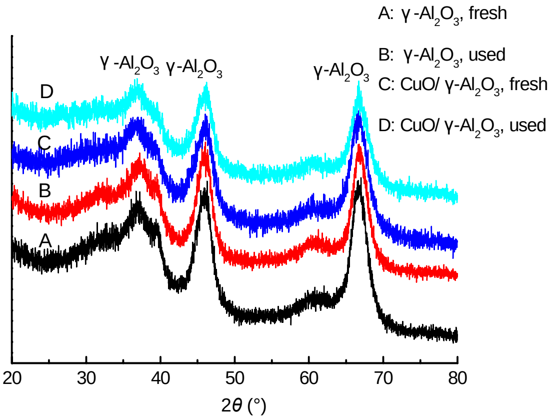

Fig. 3 Comparison of XRD patterns of catalysts before and after usage

The pore properties of the catalysts are shown in Table 1. The sol-gel-derived alumina granules had a large surface area, large pore volume and uniform pore size distribution (Buelna *et al.*, 2003). The surface area and pore volume of the CuO-coated alumina granules were lower than those of the pure alumina granules. There was no difference between the fresh and used surface areas and pore volumes (20-h test). It inferred that the catalysts had a strong capability of anti-ablation. Both the results of XRD and BET predicted that the catalysts had good structure and long lifetime.

Fig. 4 shows the result of the NH_3-TPD experiment. Ammonia started to desorb immediately when the temperature was increased, and reached the maximum at $T_{\gamma\text{-}Al_2O_3}$=473 K and $T_{CuO/\gamma\text{-}Al_2O_3}$=483 K. As desorption temperature was associated with the strength of the acid sites where NH_3 was adsorbed, a major part of the acid sites present on the surface were of rather low acid strength. However, some species were still adsorbed on the surface at high temperatures, indicating the presence of strong acid sites. The peak position did not shift obviously with copper oxide coating, indicating that the nature of acid centers were unchanged. The area of the peak was associated with the number of acid site and the area of γ-Al_2O_3 was bigger than that of CuO/γ-Al_2O_3, which was in accordance with the results of the BET experiments.

Table 1 Pore structure properties of the catalysts

Sample		BET (m^2/g)	Pore volume (cm^3/g)	Pore radius (nm)
γ-Al_2O_3	Fresh	323.8	0.581	7.18
	Used	324.4	0.587	7.24
CuO/γ-Al_2O_3	Fresh	257.5	0.497	7.72
	Used	256.1	0.497	7.74

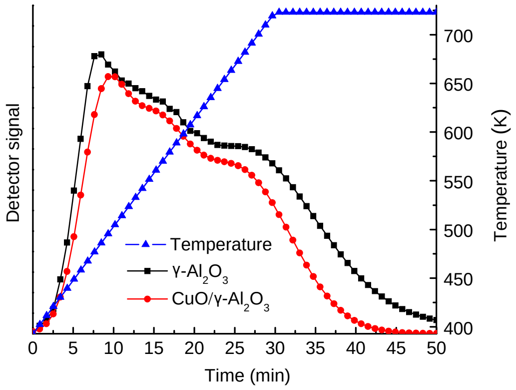

Fig. 4 NH_3-TPD experiment (100 mg of catalyst; purging gas: He; flow rate=0.03 L/min; heating ramp=11 K/min)

3.2 Thermal decomposition without catalyst

Fig. 5 shows the NH_3, HNCO, NO, and N_2O concentrations in urea-water solution decomposition without catalysts. In the case without oxygen, the amount of NH_3 plus HNCO stayed at approximately

780×10^{-6} which meant the over 90% of urea was decomposed to NH_3 and HNCO. The ratio of NH_3 to HNCO, $R_{NH_3/HNCO}$, increased from approximately 1.2 to 1.7 with increasing temperature. Our result of the ratio was consistent with the ratio obtained by Aoki *et al.* (1999) which was 1.1–1.5. Gentemann and Caton (2001) also found little HNCO converted to NH_3 in a quartz tube even in the high temperature and long resident time. But there was a big discrepancy with the results by Yim *et al.* (2004) who researched on the aluminum tube. They found large amounts of NH_3 even in the low temperature (<723 K) due to the catalytic reaction on the reactor walls (Al_2O_3 formed on the aluminum tube).

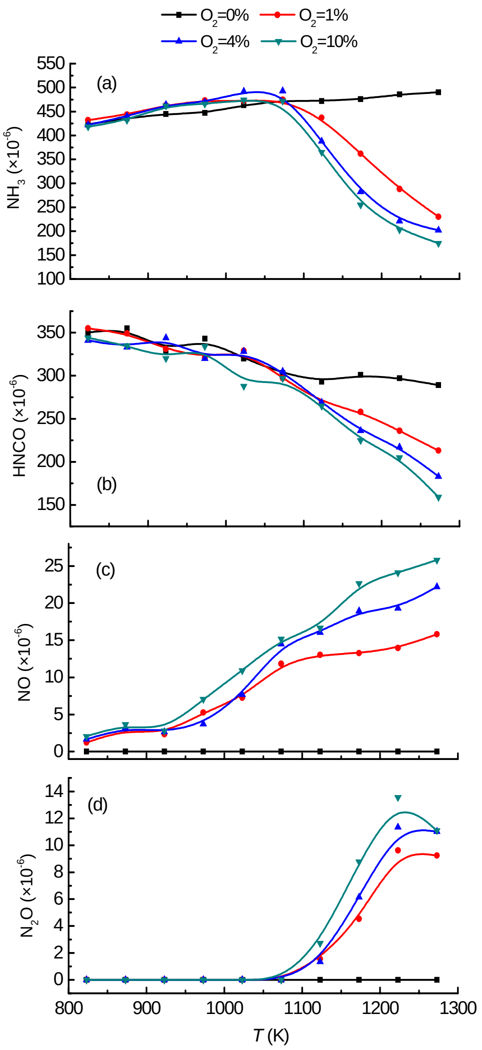

Fig. 5 Concentrations of decomposition products of urea-water solution. (a) NH_3; (b) HNCO; (c) NO; (d) N_2O
(Inlet flow composed of urea with a volume fraction 400×10^{-6}, 6% H_2O, 0%–10% O_2 and N_2 balance; flow rate=1 L/min)

When oxygen was presented in the reactor, the NH_3 and HNCO concentrations decreased with the increasing oxygen concentration above 1023 K. The NH_3 concentration decreased to approximately 190×10^{-6} and 160×10^{-6} for HNCO with oxygen concentration of 10% at 1273 K. The oxidation and reduction reaction took place at the same time. Consequently NO and N_2O were detected as the products. Figs. 5c and 5d showed the concentrations of NO and N_2O as a function of temperature, respectively. Increasing temperature or oxygen concentration resulted in higher NO production. A value of 5×10^{-6} NO was gained for 1% O_2 at 973 K which increased to 16×10^{-6} at 1273 K. The same tendency could be observed for 4% and 10% oxygen. N_2O was first observed while the temperature was above 1073 K and increased with temperature until 1223 K. The oxygen concentration had a promotive effect on the production of N_2O. The maximum production of N_2O was 14×10^{-6} for 10% O_2 at 1223 K. The results implied that N_2O production might be a problem between 1073–1223 K and the higher temperature (>1223 K) was in favor of eliminating N_2O. Since 400×10^{-6} urea was the input, 800×10^{-6} of "N" species should be produced. Besides NH_3, HNCO, NO, and N_2O, another species that concerned "N" atoms would be N_2 which was the product of SNCR reactions. In our test, N_2 could not be detected by the FTIR and its quantity would be 10×10^{-6}–200×10^{-6} calculated by N balance.

Though the HNCO hydrolysis reaction (2) was exothermic, a higher temperature rebounded to the hydrolysis. According to the Urea2000 model (Rota *et al.*, 2002) including the mechanisms and rate parameters for $DeNO_x$ and $RAPRENO_x$ processes, HNCO mainly underwent reactions (9), (3), (4), (10), and (11) without oxygen and NO:

$$\mathrm{HNCO+M\rightarrow \cdot NH+CO+M}, \tag{9}$$
$$\mathrm{HNCO+\cdot NH_2\rightarrow NH_3+\cdot NCO}, \tag{10}$$
$$\mathrm{HNCO+\cdot NH\rightarrow \cdot NH_2+\cdot NCO}. \tag{11}$$

In reaction (9), M represented N_2, O_2 or H_2O. High temperature was in favor of production of H radical and OH radical. HNCO would react with H radical to yield NH_2 radical which promoted the NH_3 formation. Since the amount of H radical and NH_3 generation increased slightly with increasing temperature, the ratio of NH_3 to HNCO increased slightly.

Fig. 6 shows the effect of vapor concentration on the decomposition of urea-water solution without oxygen. High vapor concentration was not tested in our experiments to avoid the local undercooling during water evaporation, which reduced the reactor temperature. The $R_{\mathrm{NH_3/HNCO}}$ increased slightly with increasing water concentration because more H_2O meant more H radical which helps NH_3 generation. Above 1173 K the discrepancy became smaller because the droplets evaporated so quickly and the presence of 2%–6% vapor was sufficient for HNCO hydrolysis.

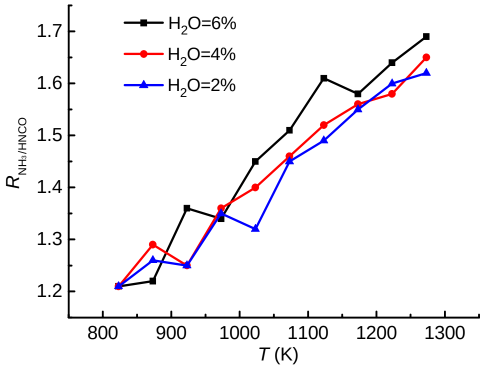

Fig. 6 Ratio of NH_3 to HNCO
(Inlet flow composed of urea with a volume fraction 400×10^{-6}, 2%–6% H_2O, 0% O_2 and N_2 balance; flow rate=1 L/min)

3.3 Catalytic performance

The activity of the catalyst for the HNCO hydrolysis could be expressed in terms of HNCO conversion as follows:

$$X_{\mathrm{HNCO}}=\left(1-\frac{C_{\mathrm{HNCO(o)}}}{C_{\mathrm{HNCO(i)}}}\right)\times 100\%, \qquad (12)$$

where X_{HNCO} was the HNCO conversion, $C_{\mathrm{HNCO(i)}}$ was the volume fraction of HNCO at the entrance of the vertical reactor while $C_{\mathrm{HNCO(o)}}$ was that for the outlet of the reactor. During the catalytic experiments, the horizontal reactor was kept at 823 K with 4% O_2 and 6% H_2O. As shown in Fig. 7, the catalysts had a great impact on the HNCO hydrolysis and the $R_{\mathrm{NH_3/HNCO}}$ was so high that it was hundred times greater than that without a catalyst. For the two catalysts the X_{HNCO} increased with temperature and there was less than 50×10^{-6} of HNCO over 473 K. The highest activity, a conversion of 98.6%, was found on pure γ-Al_2O_3 at 673 K. The X_{HNCO} decreased dramatically below 473 K. The stability of isocyanate (–NCO) groups, which came from the dissociation of HNCO on the catalysts, decreased with increasing temperature, and they were very easily removed from the surface above 473 K. Moreover, the hydrolysis of –NCO species with water to ammonia was accelerated by increasing temperature. When coated with CuO, γ-Al_2O_3 showed lower activity than pure γ-Al_2O_3. Piazzesi (2006) investigated the HNCO hydrolysis on various metal oxides and found the positive influence of the Lewis acidity of the catalysts on the HNCO hydrolysis. Pure γ-Al_2O_3 was known to have pronounced Lewis properties (Medema *et al.*, 1972). However, the addition of CuO not only reduced the surface area but also abated the Lewis acid sites as the BET and NH_3-TPD tests shown, which reduced the catalytic activity.

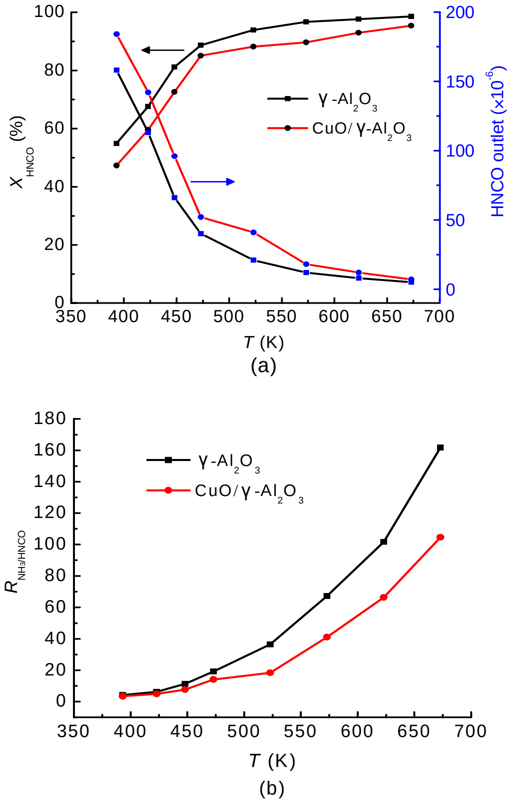

Fig. 7 Conversion of HNCO and the ratio of NH_3 to HNCO
(0.1 ml catalyst; inlet flow composed of urea with a volume fraction 400×10^{-6}, 6% H_2O, 4% O_2 and N_2 balance; flow rate=1 L/min)

Throughout the complete experiments, NO and N_2O were not detected at either the entrance or outlet of the vertical reactor. This implied that the catalysts had no catalytic function on NH_3 and HNCO oxidation.

Though the water was present in additional excess in all the experiments, the Pseudo-first order rate constants of the HNCO hydrolysis were calculated according to the rate equating to reactions under differential conditions in a plug flow reactor:

$$k_1 = -\frac{V^*}{W}\ln(1 - X_{\mathrm{HNCO}}), \tag{13}$$

where V^* is the total flow rate at actual temperature and pressure (the effect of pressure is neglected), and W is the catalyst weight. The Pseudo-first order rate constants obtained in this way for the HNCO hydrolysis were shown in Fig. 8.

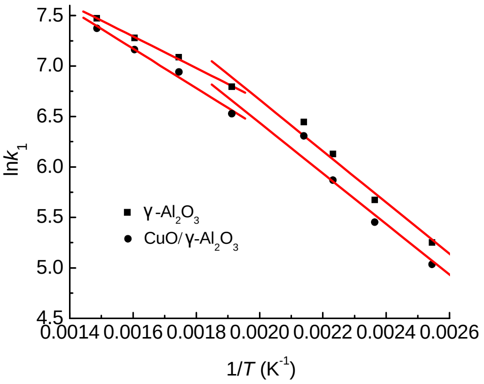

Fig. 8 Arrhenius plot for hydrolysis of HNCO

The different temperature dependence of the two rate constants could be clearly seen. When the temperature was over 473 K, the apparent activation energy of HNCO hydrolysis was approximately 13 kJ/mol for γ-Al_2O_3 while 16 kJ/mol for CuO/γ-Al_2O_3. The activation energy was so low that it suggested that the HNCO hydrolysis reaction was controlled by external diffusion. However, the energy of activation increased to 25 kJ/mol for γ-Al_2O_3 while 26 kJ/mol for CuO/γ-Al_2O_3 in the low temperature region (393–473 K). It was assumed that the hydrolysis reaction was mainly controlled by internal mass transfer within the catalyst pores.

4 Conclusions

The researches on urea-water solution thermohydrolysis were undertaken in a dual-reactor system. The high yield of HNCO showed that the HNCO was quite stable in the gas phase and difficult to convert to NH_3. In the absence of oxygen, the main products of the thermal decomposition were NH_3 and HNCO and the ratio of NH_3 to HNCO increased from approximately 1.2 to 1.7 with temperature. In the presence of oxygen, NO and N_2O as the oxidation products were clearly detected and the total amount of NH_3 and HNCO decreased dramatically above 1073 K. Higher vapor concentration in 2%–6% led to a slightly higher ratio of NH_3 to HNCO. It was indicated by chemical analysis that H radical was in favor of HNCO hydrolysis by driving the reaction $HNCO + H\cdot \rightarrow \cdot NH_2 + CO$.

The γ-Al_2O_3 catalysts made by the sol-gel method had a large surface area, pore volume, and high activity, which resulted in good catalytic effects. The catalysts enhanced HNCO hydrolysis and raised the ratio of NH_3 to HNCO to approximately one hundred. The HNCO conversion with γ-Al_2O_3 and CuO/γ-Al_2O_3 catalysts maintained above 85% above 400 K with GHSV=6×10^5 h^{-1}. The apparent activation energy of the hydrolysis reaction amounted to about 25 kJ/mol in 393–473 K while 13 kJ/mol over 473 K. The intrinsic rate of hydrolysis reaction of HNCO was so high on catalysts that the overall reaction rate was mainly determined by external and internal mass-transfer limitations. The pure γ-Al_2O_3 showed a better performance than CuO/γ-Al_2O_3. The addition of CuO not only reduced the surface area but also lessened the Lewis acid sites which were recognized to have positive effect on the catalytic activity. There was no obvious change between the fresh and used catalyst samples, which proved good structural stability of the catalysts.

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