



Conversion of Urea to Cyanamide Over Phosphorus-Modified H-ZSM-5

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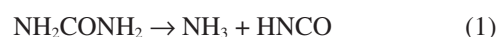
A novel high active catalyst for the decomposition of urea into cyanamide was developed by treating H-ZSM-5 zeolite with phosphoric acid solution. The catalytic activity of the phosphorous modified H-ZSM-5 was tested in a continuous flow fixed bed reactor at 823 K and atmospheric pressure. The acidity of catalysts, especially Brønsted acid sites, is decreased by phosphorous modification. The selectivity for cyanamide of the catalysts is enhanced by the addition of phosphorus component. These results indicate that the Brønsted acid sites strength is a crucial factor for the selective production of cyanamide.

Keywords: H-ZSM-5, Cyanamide, Urea, Modification, H₃PO₄.

INTRODUCTION

Cyanamide [$\text{H}_2\text{N}-\text{C}\equiv\text{N}$] was first obtained by Bineau¹ from cyanogen chloride and ammonia in 1838. It is a very important organic chemical intermediate in the production of fertilizers, plant protection agents, pharmaceuticals, biocides, dyestuffs and a number of other valuable fine chemicals^{2,3}. Currently, cyanamide is being widely produced by the hydrolysis process from calcium cyanamide⁴. However, calcium cyanamide is produced from limestone, coke and nitrogen which leads to large amounts of energy consumption, also often contains large number of impurities and copious waste. At the same time, the calcium cyanamide hydrolysis process generates a large number of calcium carbonate which is environmentally undesirable.

In the past decades, many green methods had been developed for producing cyanamide. Boatright and Mackay⁵ prepared cyanamide from ammonia and carbon dioxide at temperatures of between 350 and 800 °C in the presence of a porous inorganic oxide gel having a large surface area. A considerable amount of undesired product, melamine, was formed by trimerization of cyanamide in this process. Furthermore, Hardeveld *et al.*⁶ proposed a process for the preparation of cyanamide by passing urea over catalyst at a temperature in the range of between about 200 and 600 °C. Ammonia was used as fluidizing gas and as entraining gas. At first, urea (NH₂CONH₂) decompose to equimolar amounts of ammonia and isocyanic acid (HNCO) (eqn. 1). Then, isocyanic acid/cyanic acid reacts with ammonia to form cyanamide (NH₂CN) (eqn. 2).



A porous catalyst was utilized which has an intracrystalline pore diameter of at most 8 Å in this process, whereby the formation of melamine byproducts was substantially reduced. However, only conversions of urea at most 36.3 % were achieved. A similar process was also described by Weitkamp *et al.*^{7,8}. Zeolites ZSM-5, Na-Y, H-Y and β exchanged by transition metal cations were used as catalysts. In recent years, many researchers have been engaged in studying urea thermolysis (eqn. 2) since urea is widely used in flue gas denitrification as a reducing agent, especially in automobile diesel applications⁹⁻¹³. ZSM-5 zeolite is one of the most well-known solid acid catalysts which are found to be highly active for urea thermolysis. However, there is little information available in the literature about the production cyanamide from urea over ZSM-5.

In the present work, influences of phosphorus modification on the catalytic performance of modified H-ZSM-5 catalysts for the decomposition of urea to produce cyanamide were investigated. To the best of our knowledge, this is the first study about the production of cyanamide from urea decomposition over phosphorus-modified H-ZSM-5 catalysts. The catalysts were characterized by different techniques including X-ray diffraction (XRD), nitrogen adsorption-desorption isotherms, pyridine-adsorption FT-IR (Py-IR).

EXPERIMENTAL

Catalyst preparation: Phosphorus-modified commercial H-ZSM-5 (SiO₂/Al₂O₃ = 38, Nankai University catalyst Co.,

Ltd., China.) samples were treated by aqueous solution of H_3PO_4 . H-ZSM-5 powder (50 g) was dispersed in 500 mL of aqueous solution of H_3PO_4 (0.12-0.47 M) under stirring. The mixture was heated to 353 K and kept at this temperature for 3 h and then the solid was filtrated, washed by deionized water and dried at 393 K for 12 h. Then the samples were pelletized, crushed and sieved to 20-40 mesh. Finally, the samples were calcined at 823 K for 6 h in a current of nitrogen. The modified samples were marked as "xP-ZSM-5", where x denotes the concentration of the H_3PO_4 solution using for phosphorus modification.

X-ray diffraction (XRD) patterns were measured by a Bruker D8-Focus X-ray diffractometer at a scanning speed of $4^\circ/\text{min}$, with CuK_α radiation operated at 40 kV and 40 mA. The 2-theta value was scanned in the range of $5\text{-}50^\circ$. Nitrogen adsorption-desorption isotherms were measured at 77 K with a Quantachrome autosorb iQ apparatus. Specific surface areas were calculated following the Brunauer-Emmett-Teller (BET) and pore volume were obtained from the amount of nitrogen adsorbed by the samples at $p/p_0 = 0.995$. The acid sites (Brønsted and Lewis) were determined by the pyridine-adsorption FT-IR spectrometry. Self-supporting wafers (12 mm diameter) were made from 20 mg of zeolite. The wafers were pre-heated at 673 K for 1 h in the cell at 0.1 Pa and then, after cooling to 333 K, the pyridine vapor was introduced. After degassing the excess pyridine, IR spectra of adsorbed pyridine of the samples were recorded with Bruker VERTEX 70 spectrometer at 423 K and 573 K.

Catalytic test: The experiments were carried out in a fixed-bed continuous flow quartz reactor at atmospheric pressure. The electric furnace provided required temperature (823 K) and 15 mL catalyst was loaded into the quartz tube reactor. A desired amount of urea (5 g/h) was continuously fed into the reactor using a trace feeder and then the urea evaporates and thereby decomposes to a mixture of isocyanic acid. The gas mixture produced in this way was passed through the bed of catalyst. The main products including cyanamide, dicyandiamide and melamine were condensed out at 253 K in a condenser directly behind the reactor. Urea, dicyandiamide and melamine were analyzed off-line by HPLC (Lab Alliance Model 5250) using Kromasil C18 column ($5\ \mu\text{m} \times 250\ \text{mm} \times 4.6\ \text{mm}$) and detector UV 200nm, the eluent was 0.25 wt. % ammonia aqueous solution. Cyanamide was determined by titration method¹⁴.

RESULTS AND DISCUSSION

X-ray diffraction patterns of parent and phosphorus modified H-ZSM-5 samples are given in Fig. 1. It can be seen that the well-crystalline MFI structure is preserved in phosphorus modified samples. It is suggested that modification by phosphorus has no effect on the basic phase structure of the H-ZSM-5 zeolites. However, the relative crystallinity (Table-1) decreases with increasing concentration of H_3PO_4 solution, probably due to partial dealumination of H-ZSM-5 without intensively destroying the lattice structure¹⁵⁻¹⁹.

N_2 physisorption results of parent and phosphorus modified H-ZSM-5 catalysts are presented in Table-1. The BET surface area of the phosphorus modified H-ZSM-5 samples

is continuously decreased as the incorporation of phosphorus. But the pore volume is increased first and then decreased with H_3PO_4 treatment. This may be explained by the fact that the treatment with dilute H_3PO_4 only clears the amorphous particles in the pores leading to the pore volume slight increase. However, higher concentration of H_3PO_4 treatment dissolves a part of pore walls resulting in the formation of wider pores. Besides, the higher concentration of H_3PO_4 concentration treatment may also form polymeric phosphates species, especially at the entrance of pore channels¹⁹. Thus the surface areas and pore volume decrease obviously.

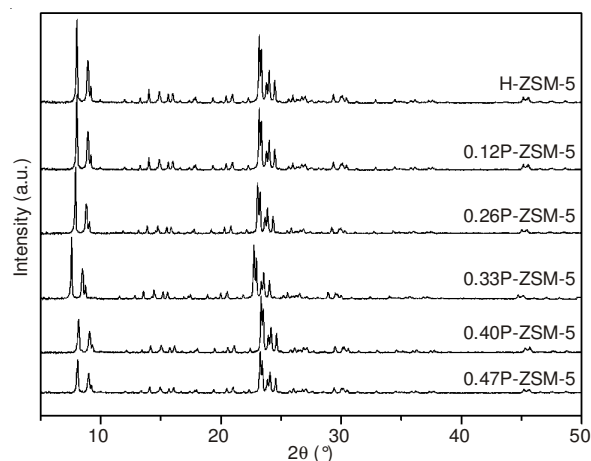


Fig. 1. XRD patterns of parent H-ZSM-5 and phosphorus modified H-ZSM-5

TABLE-1
PHYSICAL PROPERTIES OF PARENT HZSM-5
AND PHOSPHOROUS MODIFIED HZSM-5

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	XRD (%) ^a
H-ZSM-5	411	0.2006	100
0.12P-ZSM-5	402	0.2113	91
0.26P-ZSM-5	381	0.1991	74
0.33P-ZSM-5	332	0.1639	73
0.40P-ZSM-5	307	0.1580	70
0.47P-ZSM-5	304	0.1531	57

^a The relative crystallinity

The variations of the acidic properties of phosphorus modified H-ZSM-5 samples were characterized by Py-IR at 423 K and 573 K, as shown in Fig. 2. The spectra at 423 K and 573 K represent the properties of the total and strong acid sites, respectively. The band at $1545\ \text{cm}^{-1}$ that is usually assigned to pyridine molecules adsorbed on Brønsted acid sites, as well as the band at $1450\ \text{cm}^{-1}$ that is usually assigned to pyridine molecules adsorbed on and Lewis acid sites. The amounts of Brønsted and Lewis acid sites were determined from the integrated areas of the bands at $1545\ \text{cm}^{-1}$ and $1450\ \text{cm}^{-1}$, respectively, using the method reported by Emeis²⁰ and presented in Table-2. Most of the acid sites among both total (weak and strong) and strong acid sites in both parent H-ZSM-5 and phosphorus modified H-ZSM-5 samples are of the Brønsted type (the minimum of the ratio of Brønsted acidic sites to Lewis acidic sites (B/L) is 9 (Table-2)). For the properties of total acid sites, the intensity of both Brønsted and Lewis acid sites decrease with the increasing H_3PO_4 concentration when the

TABLE-2
ACID DENSITY OF PARENT HZSM-5 AND PHOSPHOROUS MODIFIED HZSM-5

Sample	Density of acid sites ($\mu\text{mol/g}$)								B573/B423
	423 K-desorption				573 K-desorption				
	Total ^c	B ^a	L ^b	B/L	Total ^c	B ^a	L ^b	B/L	
H-ZSM-5	39	36	3	12	5.1	5	0.1	50	0.14
0.12P-ZSM-5	20	18	2	9	4.03	4	0.03	133	0.22
0.26P-ZSM-5	14	13	1	13	3.02	3	0.02	150	0.23
0.33P-ZSM-5	9.3	9	0.3	31	2.008	2	0.008	250	0.22
0.40P-ZSM-5	38	36	2	18	4.02	4	0.2	200	0.11
0.47P-ZSM-5	42	40	2	20	4.03	4	0.03	133	0.1

^aB: Brønsted; ^bL: Lewis; ^cTotal = B + L; The number after B and L refers to pyridine desorption temperature (in K)

H_3PO_4 concentration is lower than 0.33 M, while it begins to increase with further increasing H_3PO_4 concentration (Fig. 2 (a)). The change in both Brønsted and Lewis acid sites presents same trends depending on H_3PO_4 treatment for the properties of the strong acid sites as that of total acid sites. The weakening in acid sites may be attributed to be the results of dealumination of ZSM-5 framework during low concentration H_3PO_4 treatment^{15-19, 21-23}. With the increasing concentration of H_3PO_4 , new acid sites may be formed due to the formation of polymeric phosphates species which enhances acid intensity of phosphorus modified H-ZSM-5 samples^{18,21}.

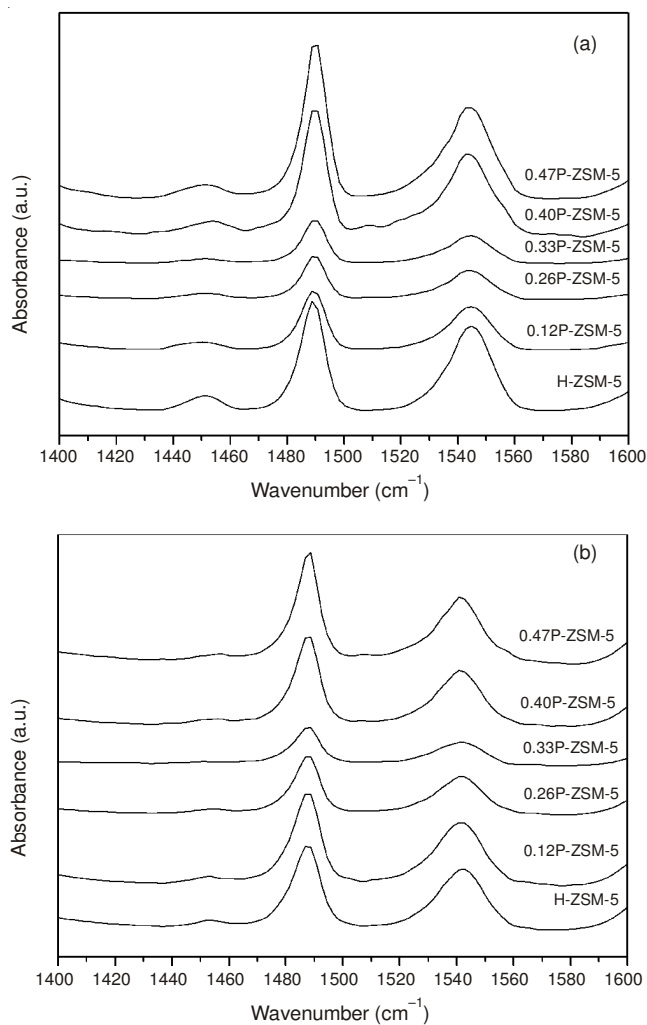


Fig. 2. Pyridine-absorbed FTIR spectra of parent HZSM-5 and phosphorus modified HZSM-5, (a) 423 K, (b) 573K

There is only Brønsted acid sites among strong acid sites in phosphorus modified H-ZSM-5 samples, because Lewis acid sites almost completely disappear [Fig. 2 (b)]. Furthermore, the most of the Brønsted acid sites exist in the form of weak acid type as inferred from the respective B573/B423 ratios shown in Table-2.

Catalytic activity: Fig. 3 shows the dependence of urea conversion and selectivity towards cyanamide on parent H-ZSM-5 catalyst and various phosphorus modified H-ZSM-5 catalysts at 823 K. As shown in Fig. 3(a), phosphorus modification has no effect on the conversion of urea. About 90 % conversion of urea is achieved on parent H-ZSM-5 and all phosphorus modified H-ZSM-5 catalysts. Urea decomposition on the H-ZSM-5 catalyst at 823 K shows main products

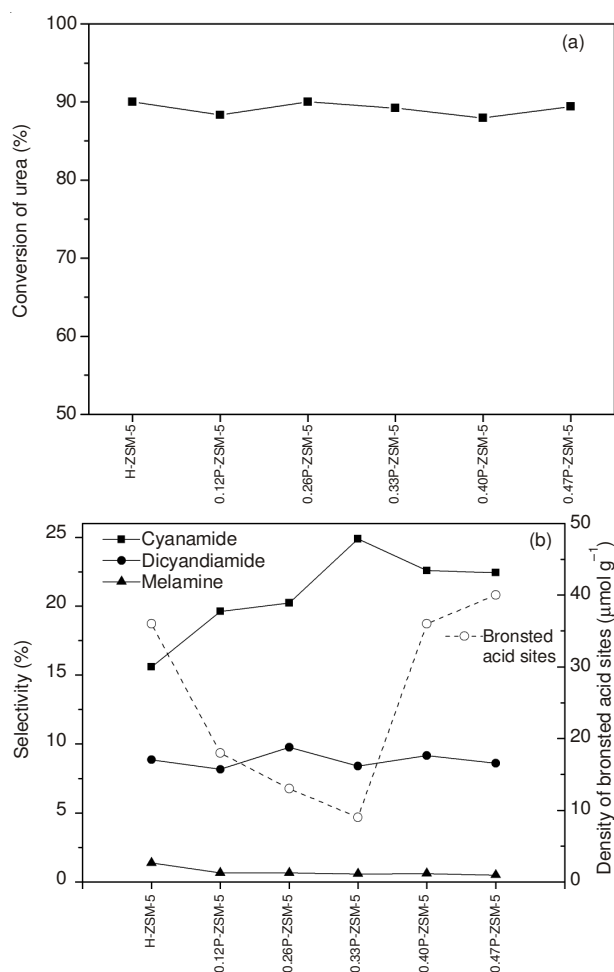


Fig. 3. Catalytic performances of parent H-ZSM-5 and phosphorus modified H-ZSM-5

including cyanamide, dicyandiamide and melamine. In Fig. 3 (b) the selectivity towards cyanamide on phosphorus modified H-ZSM-5 catalysts is higher than that of parent H-ZSM-5 catalyst and increased significantly with the increasing H_3PO_4 concentration when the H_3PO_4 concentration was lower than 0.33 M and then decreased gradually with further increasing H_3PO_4 concentration. Obviously, the change of surface acidity, especially Brønsted acid site, plays an important role on increase of selectivity towards cyanamide. The increase in cyanamide selectivity can be ascribed mainly to the decreased Brønsted acid site strength and density due to H_3PO_4 treatment [Fig. 3 (b)]. In contrast, the increase of Brønsted acid sites strength and density results in the decrease in cyanamide selectivity since more Brønsted acid sites will promote the urea decomposition to form carbon dioxide and ammonia¹⁰. Both selectivity of dicyandiamide and melamine are slightly reduced due to the decrease of surface area and pore volume⁶. Seemingly, the sum of the products selectivity is less than 100 %. It is due to hydrolysis intermediate of urea, isocyanic acid and cyanic acid, which are quite stable in the gas phase but easily react with gas phase water to produce large amounts of carbon dioxide and ammonia⁹.

Conclusion

Phosphorus modified H-ZSM-5 catalysts prepared by H_3PO_4 solution treatment show higher activity in urea decomposition to produce cyanamide. Phosphorus modification leads to decrease in both surface and pore volume and does not bring about destroying the framework structure of H-ZSM-5. The intensity and density of Brønsted acid sites among both total and strong acid sites is decreased by relative dilute H_3PO_4 treatment. The change in the acidity has great influences on the catalytic performance of phosphorus modified H-ZSM-5 samples. The selectivity for cyanamide increases with the decrease in the intensity and density of Brønsted acid sites, while urea conversion is irrelative to the acidity of catalysts.

REFERENCES

1. K.D. Wehrstedt, W. Wildner, T. GÜthner, K. Holzrichter, B. Mertschenk and A. Ulrich, *J. Hazard. Mater.*, **170**, 829 (2009).
2. D. Dierolf, S. Scheitza, J. Bonifas and B. Blömeke, *Toxicol.*, **302**, 1 (2012).
3. H. Niederhofer, W. Staffen and A. Muir, *Alcohol*, **38**, 50 (2003).
4. T. Guthner and B. Mertschenk, Cyanamides, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, edn 7 (2011).
5. L.G. Boatright and J.S. Mackay, US Patent 2,721,786 (1955).
6. R. van Hardeveld, T.J. van de Mond and F.H.A.M.J. Vandenbooren, US Patent 4,625,061 (1986).
7. J. Weitkamp, S. Ernst, H. Rock, K. Scheinost, B. Hammer, W. Goll and H. Michaud, US Patent 5,166,432 (1992).
8. J. Weitkamp, B. Hammer, W. Goll and H. Rock, DE Patent #4001805A1 (1991).
9. W. Yang, Z. Chen, J. Zhou, Z. Huang and K. Cen, *Ind. Eng. Chem. Res.*, **50**, 7990 (2011).
10. J.A. Sullivan and O. Keane, *Appl. Catal. B*, **61**, 244 (2005).
11. P.M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach and J. Brauer, *Thermochim. Acta*, **424**, 131 (2004).
12. M. Eichelbaum, A.B. Siemer, R.J. Farrauto and M.J. Castaldi, *Appl. Catal. B*, **97**, 98 (2010).
13. L. Olsson, H. Sjøvall and R.J. Blint, *Appl. Catal. B*, **87**, 200 (2009).
14. L.A. Pinck, *Ind. Eng. Chem.*, **17**, 459 (1925).
15. J. Lu and Y. Liu, *J. Nat. Gas Chem.*, **20**, 162 (2011).
16. K. Ramesh, L. Hui, Y. Han and A. Borgna, *Borgna. Catal. Commun.*, **10**, 567 (2009).
17. J. Schulz and F. Bandermann, *Chem. Eng. Technol.*, **17**, 179 (1994).
18. N. Xue, X. Chen, L. Nie, X. Guo, W. Ding, Y. Chen, M. Gu and Z. Xie, *J. Catal.*, **248**, 20 (2007).
19. K. Ramesh, C. Jie, Y. Han and A. Borgna, *Ind. Eng. Chem. Res.*, **49**, 4080 (2010).
20. C.A. Emeis, *J. Catal.*, **141**, 347 (1993).
21. A. Rahman, G. Lemay, A. Adont and S. Kaliaguine, *J. Catal.*, **112**, 453 (1988).
22. Z. Song, A. Takahashi, I. Nakamura and T. Fujitani, *Appl. Catal. A*, **384**, 201 (2010).
23. A. Takahashi, W. Xia, I. Nakamura, H. Shimada and T. Fujitani, *Appl. Catal. A*, **423-424**, 162 (2012).