Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S195-S197

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19044

Study on HNCO Hydrolysis and Reduction in Marine Urea-SCR Systems

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Published online: 24 December 2014; AJC-16469

HNCO is an important composition in chemical reaction processes in marine Urea-SCR systems. This paper reported on HNCO hydrolysis and reduction in marine Urea-SCR systems. Firstly, by using different catalysts, this paper carried out the experimental study on the catalytic hydrolysis process of HNCO, the effects of different catalysts on HNCO hydrolysis and the actions of varied parameters together with NH_3 on HNCO hydrolysis. As results, the optimal operation conditions of HNCO hydrolysis were obtained. Secondly, by using HNCO as a reductant, the paper carried out the HNCO reduction experiments to analyze the denitration rate under varied test parameters. While by comparing the effects on reduction process of NH_3 reductant, the regulations of HNCO reduction reactions were drawn. The results are of important reference value for the further research of ship Urea-SCR technology and are helpful in further optimizing Urea-SCR systems.

Keywords: Marine Urea-SCR system, HNCO, Hydrolysis, Reduction.

INTRODUCTION

With the IMO emission regulations for marine diesel engine NO_x emission limitsbeing increasingly strict, in order to control ship diesel engine NO_x emissionseffectively, it is imperative to strengthen the NO_x emission control technology research[1,2]. As an effective exhaust after treatment method, selective catalytic reduction (SCR) technology is a denitration method which is currently the most widely used. Among them, the urea-SCR technology has become the most effective technology for ship diesel engine to meet emission regulations, and HNCO is an important part of the urea-SCR technology, affecting the efficiency of urea use and NO_x removal efficiency, even influence the SCR systems security. Therefore HNCO is an important ring of the ship urea-SCR technology.

EXPERIMENTAL

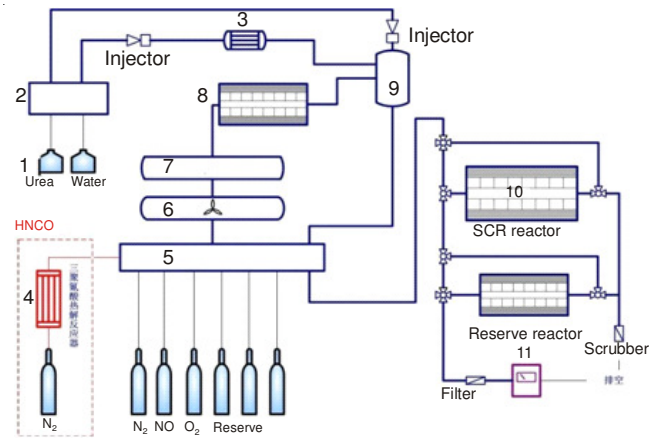
The improved physical SCR bench is shown in Fig. 1 while an improved system diagram of the experimental system SCR is shown in Fig. 2.

The reaction generator of HNCO is connected to the SCR system, together along with the electronic temperature control system, to make it a relatively independent pipeline of new reactions from other pipeline. The carrier gas N_2 need to pick another cylinder to generate a separate gas line; The catalyst was placed into the SCR reactor; When the pyrolysis reaction takes place in the preparing reaction generator of HNCO, a stable stream of HNCO generated will enter SCR bench pipeline by the carrier gas of N_2. The flow passes into the flue gas analyzer at No. 11 which records concentration of various gases and then the degree of catalytic hydrolysis and reduction results of HNCO obtained.

Fig. 1. Improved SCR bench

RESULTS AND DISCUSSION

Comparative analysis of catalyst hydrolysis properties: The changes of promotion and improving rate is shown in Fig. 3 that the four kinds of catalysts supported TiO_2, extruded V_2O_5-WO_3/TiO_2, supported V_2O_5-WO_3/TiO_2 and supported CuO/TiO_2 have on HNCO hydrolysis reaction.



1. Water jet pump; 2. Water pressure flowmeter; 3. Carburator; 4. HNCO reaction generator; 5. Gas pressure flowmeter; 6. Gas dynamic mixer; 7. Gas cushion; 8. Mixed gas preheater; 9. Gas and water mixer; 10. The SCR reactor; 11. Flue gas analyzer

Fig. 2. Improved SCR system diagram

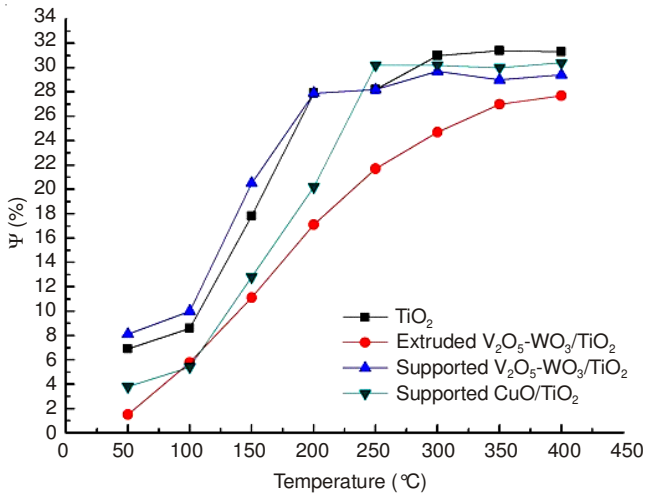


Fig. 3. Changes of promotion and improving rate

TiO_2 has the best catalyzed effecton promoting the hydrolysis reaction of HNCO, followed by the supported CuO/TiO_2 catalyst and supported V_2O_5-WO_3/TiO_2 catalyst, extruded V_2O_5-WO_3/TiO_2 catalyst worst. With increasing temperature, the improvement rate is the fastest that TiO_2 and supported V_2O_5-WO_3/TiO_2 has effect on hydrolysis reaction of HNCO, extruded V_2O_5-WO_3/TiO_2 slowest. In the range of 350-400 °C, the hydrolytic activity of four kinds of catalysts are substantially unchanged, indicating that 350-400 °C is the best catalytic hydrolysis temperature for the catalysts; Active ingredient of the two catalysts supported V_2O_5-WO_3/TiO_2 and extrusion-type V_2O_5-WO_3/TiO_2 is same, but due to the different preparation process, V_2O_5 loading of the latter is higher than the former. The promoting and improving rate for HNCO hydrolysis reaction by the extruded V_2O_5-WO_3/TiO_2 catalysts is far lower than that by the supported V_2O_5-WO_3/TiO_2 catalysts, thus explained, with the increase of V_2O_5 catalyst loading catalysis, the catalytic action for HNCO hydrolysis weakens on the contrary[3,4].

Effect of NH_3 component on the HNCO catalytic hydrolysis reaction: In the actual working conditions of Urea-SCR system, the hydrolysis reaction of HNCO often takes place in the circumstance of an excess NH_3. To further investigate the characteristics of HNCO hydrolysis reaction in the practical application, NH_3 continues to pass into reactor while carrying HNCO catalyzed hydrolysis test, then to study the influence of NH_3 on HNCO catalyzed hydrolysis reactions.

In the study of the effect of NH_3 on HNCO catalyzed hydrolysis reaction, TiO_2 is selected as the catalyst. 500 ppm NH_3 was thrown into the system in the testing process. The specific test results are described in Table-1.

TABLE-1
EFFECTS OF NH_3 ON HNCO HYDROLYSIS REACTION

Temperature (°C)	NH_3 concentration before water injection (ppm)	NH_3 concentration after water injection (ppm)	The HNCO concentration (ppm)
50	94	848	754
100	92	852	760
150	91	897	806
200	98	994	896
250	87	1012	925
300	103	1047	944
350	92	1055	963
400	101	1067	966

The degree of HNCO hydrolysis with NH_3 injected is shown in Table-2. The tends that the degree of HNCO hydrolysis changes with the temperature is shown in Fig. 4.

TABLE-2
DEGREE OF HNCO HYDROLYSIS WITH NH_3

Temperature (°C)	Concentration of HNCO in catalytic hydrolysis (ppm)	Concentration of HNCO in non catalytic hydrolysis (ppm)	Concentration difference (ppm)
50	754	741	13
100	760		19
150	806		65
200	896		155
250	925		184
300	944		203
350	963		222
400	966		225

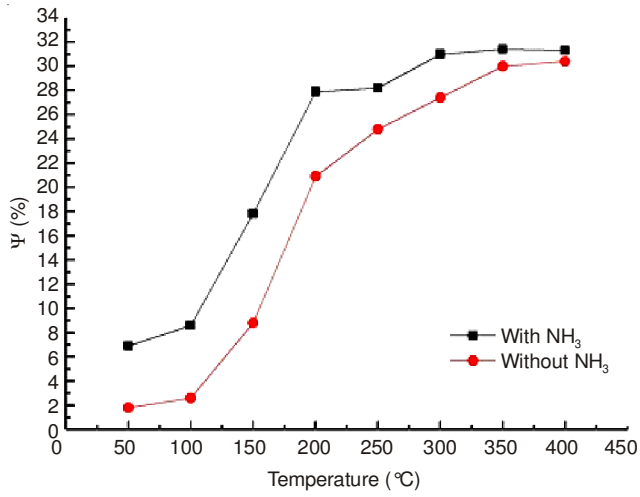


Fig. 4. Increase rate of HNCO hydrolysis with NH_3 injected

From Fig. 5, it can be found that in the temperature 350 °C, the degree of HNCO hydrolysis with excessive NH_3 is less than that without excess NH_3. But the trend of both are the same, this is because both share the same kind of catalyst; when the temperature rises above 350 °C, both basically approach, explaining that in the high-temperature conditions, the excess NH_3 for HNCO hydrolysis inhibition will be weakened until it disappears.

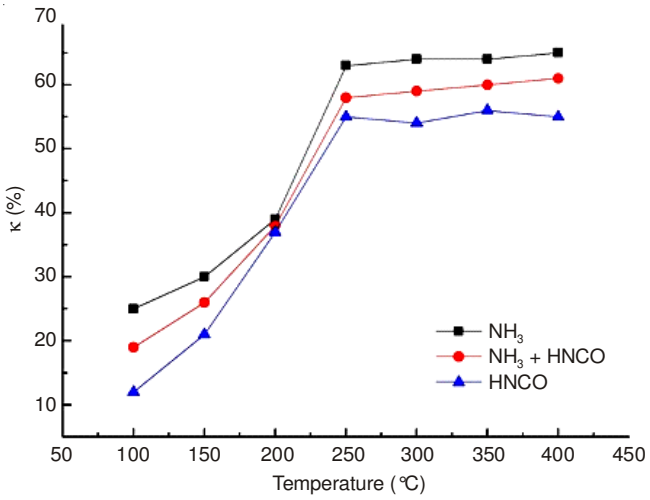


Fig. 5. Denitrification efficiency with increasing temperature

Comparative analysis of NH_3 and HNCO reduction: Taking the extrusion-type V_2O_5-WO_3/TiO_2 catalyst as example, three test results with reducer NH_3, HNCO and HNCO + NH_3 will be integrated into a map that shows the denitration efficiency with increasing temperature.

The denitration efficiency with NH_3 as the reducing agent is highest both in the low-temperature (100-200 °C) and high temperature section (200-400 °C). The reduction of HNCO is lowest with the denitration efficiency less than 60 %; HNCO + NH_3 as the reducing agent, denitrification rates in between NH_3 and HNCO; The denitration efficiency of the three tends to be the same at 200 °C, but when the temperature exceeds 200 °C, the denitration efficiency of NH_3 rises faster and then tends stable after 300 °C; The HNCO denitration efficiency rise fastest in the range of 100-200 °C, but when the temperature rises above 250 °C, the reduction of HNCO is gradually weakened.

Conclusions

• The catalytic effect is the best with only the catalyst loading TiO_2, with the increasing V_2O_5 component on the TiO_2 loading, the catalysis for the hydrolysis reaction of HNCO is gradually weakened.

• Excess NH_3 has inhibition action on HNCO catalytic hydrolysis, but the inhibition gradually disappeares over the temperature 350 °C.

• The denitration efficiency of HNCO is lower than NH_3 with the denitration efficiency of less than 60 %; the denitration efficiency is between NH_3 and HNCO with HNCO + NH_3 as the reducing agent.

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