HCN + NO_2 reaction on Na-and Ba-Y: *in-situ* FT-IR and TPD/TPR

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Introduction

The reduction of environmentally harmful NO_x gases produced by internal combustion engines is a challenging task, in particular, when the engines are operating under lean conditions, i.e. in the presence of excess oxygen. Non-thermal plasma assisted selective catalytic NO_x reduction is one the new technologies that has emerged in the past several years as a potential candidate for diesel engine exhaust control. Previous studies in our laboratory [1] have shown that alkali and alkaline earth ion exchanged Y,FAU (Y) zeolites are effective catalysts for the selective reduction of NO_x when they are used in conjunction with non-thermal plasma. In this process, the formation of a small amount of toxic HCN was reported. In our FT-IR investigation of the acetaldehyde+NO_2 reaction, we also confirmed the formation of both HCN and HNCO over Na-, and Ba-Y zeolites [2]. But, the formation and reactivities of these species toward other reactants have not been studied yet. The fundamental question is whether these species are important intermediates in the overall mechanism or just byproducts.

In this presentation, we will report the results of a study that aimed at answering this question. We investigated the adsorption of HCN on both Na-, and Ba-Y zeolites, and subsequently, the reactions that take place between HCN and NO_2 on these catalysts, using FTIR and TPD/TPR techniques.

Experimental

The materials used in this study were Na-, and Ba-Y zeolites. NaY was used as received from Zeolyst International (CBV-100), and Ba-Y samples were prepared according to the method described in our previous paper [1]. The FTIR experiments were carried out in transmission mode using a Mattson Research Series spectrometer operated at 4 cm^{-1} resolution, and each spectrum was the average of 64 scans. A UTI 100 mass spectrometer connected to the IR cell was used to analyze gas composition and the desorbing species during TPD experiments.

Results and Discussion

Fig.1 shows a series of IR spectra obtained from the HCN + NO_2 reaction over a Ba-Y zeolite. The intensities of the IR bands of adsorbed HCN (2107cm^{-1}) and NO^+ (2050cm^{-1}) decreased gradually with reaction time. Parallel to these changes, the intensities of new IR features increased. These new features can be assigned to N_2O (2245 cm^{-1}), CN^- (2165 and 2148 cm^{-1}), NCO^- (2288 ~ 2262 cm^{-1}) and CO_2 (2354 cm^{-1}). The observed IR features are consistent with the oxidation of HCN over Na- and Ba-Y by NO_2

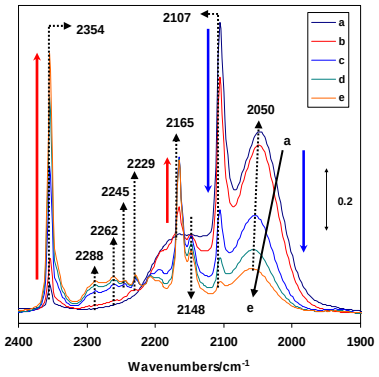

Fig. 1 HCN +NO_2 reaction over Ba-Y. [295K(a); 373K, 16 min(b); 473K. 1 min(c); 473K, 6 min(d); 473K, 16 min(e); HCN/NO_2 = 2]

$$2HCN + NO_2 \rightarrow H_2O + 2CN + 2NO \quad (1)$$
$$CN + NO_2 \rightarrow N_2 + CO_2 \text{ or } N_2O + CO \quad (2)$$

The formation of N_2, N_2O, NO, CO, and CO_2 were confirmed by the gas phase analysis conducted both prior to and following the high temperature reactions, using a mass spectrometer.

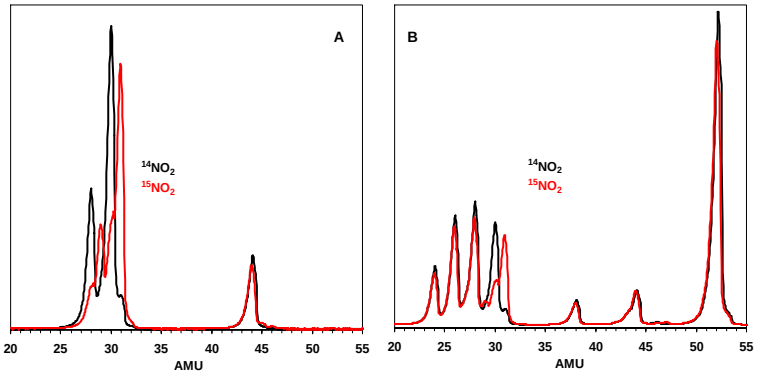

Fig. 2 MS analysis of the gas phase after HCN + NO_2 reaction at 473K for 10 min(A) and after 5 min evacuation at 300K(B). [Ba-Y, HCN/NO_2 = 2]

In order to differentiate between N_2 and CO gas-phase products, these experiments were carried out using both $^{14}NO_2$ and $^{15}NO_2$. Fig. 2(A) shows a large increase in the intensity of the 29 amu peak when the reaction is carried out with $^{15}NO_2$, suggesting the formation of a significant amount of $^{15}N^{14}N$. These results suggest the formation of a significant amount of N_2 and CO_2 as a result of reaction between HCN + NO_2, in accordance with the reaction sequence proposed above. After evacuation of the cell, new species desorbing from catalysts are observed (Fig.2 (B)). In particular, the peak at 52 amu is noteworthy, since it suggests the formation of C_2N_2. Following the initial hydrogen abstraction from HCN, adsorbed CN forms which subsequently can dimerize to produce C_2N_2.

The results of this investigation strongly suggest that HCN/CN can be an important intermediate in the overall NOx reduction on these zeolite catalysts as their reaction with ionic NOx species can lead to the formation of N-N bonds.

References

1. Kwak, J. H., Szanyi, J., and Peden, C.H.F., *J. Catal*. **220**, 291(2003), and references therein.
2. Szanyi, J., Kwak, J.H., Moline, R.A., and Peden, C.H.F., *J. Phys. Chem*. B, **108**, 17050 (2004).