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Selective catalytic combustion of hydrogen cyanide over metal modified zeolite catalysts: From experiment to theory

Ning Liu^{a,b}, Xiaoning Yuan^a, Biaohua Chen^a, Yingxia Li^{a,c}, Runduo Zhang^{a,c,*}

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, China

^b Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou, 213164, China

^c Beijing Key Laboratory of Energy Environmental Catalysis, Beijing University of Chemical Technology, Beijing, 100029, China

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ABSTRACT

A series of metal modified zeolite including Cu-(Beta, FER, MCM-22, MCM-49, MOR) and M-(M = Cu, Co, Fe, Mn, Ni)-ZSM-5 was prepared by impregnation method and characterized by BET, XRD, and H₂-TPR. HCN-SCC (selective catalytic combustion) activity measurement results suggest that Cu-ZSM-5 exhibiting excellent HCN conversion activity (T₉₀ = 350 °C) and N₂ yield (> 95% at T > 350 °C) constitutes one kind of promising candidate for HCN catalytic abatement. The HCN-SCC mechanism was further investigated by density functional theory (DFT) over constructed 20T-Cu-ZSM-5 models, which suggests that: (i) the 20T-Cu-ZSM-5 containing double active [Cu]⁺ site was much more favorable than that of 20T-Cu-ZSM-5 with single active [Cu]⁺ site during NCO generation step, being mainly related to the cooperation effect of double active [Cu]⁺ site; (ii) NCO + NO → N₂ + CO₂ was confirmed to be the one kind of probable reaction pathway for N₂ and CO₂ generations, wherein the NO could be produced through oxidation of NCO; (iii) the DFT energy calculation results as well as the microkinetic analyses suggested that the NCO formation step possessing the highest energy barrier (10.4 kcal mol⁻¹) was proposed to be the rate determining step of the whole catalytic cycle.

1. Introduction

Hydrogen cyanide (HCN), being of one kind of highly toxic N-containing volatile organic compounds (VOCs), can be largely released from the effluents of acrylonitrile and carbon fiber plants, which exerts great threat to the human health [1]. As reported [2], the intoxication mechanism of HCN is similar to that of CO, but its toxicity is 35 times higher than that of CO. Therefore, it is an urgent and obligatory business to prevent its emission into the atmosphere. Incineration method is widely utilized in the conventional VOCs abatement, such as benzene, alkane, alkene and other hydrocarbon exhausts. However, as for N-containing VOCs (HCN, CH₃CN, C₂H₃CN) the high-temperature treatment can readily produce large amounts of NO_x, resulting in a secondary air pollution problem. Therefore, the traditional VOCs treatment method of incineration is not suitable for the N-containing VOCs abatement.

Selectively catalytic combustion (SCC) could transform the nitrile gases [HCN, CH₃CN, C₂H₃CN (AN)] into harmless products of N₂, CO₂ and H₂O under low temperature ranges of 200–400 °C, which has attracted great attentions of the environmental catalysis communities [3–11]. The catalysts being involved in this reaction system mainly

include noble metal catalysts (Pd, Pt) [3,4], metal oxide catalysts [MO_x (M = Mg, Ca, Mn, Fe, Co, Ni, Cu and Zn, Ga)] [5], and zeolite catalysts [4,6–10]. As reported, although the noble metal catalyst (Pd, Pt) possesses high catalytic activity, its poor N₂ selectivity (< 20%) as well as high cost greatly hindered its wide application [3,4]. The metal oxide catalyst possesses relatively higher N₂ selectivity (20%–40%) than that of noble metal catalyst [5], but this is still hard to meet the increasingly strict NO_x emission legislation.

Recently, it was found that zeolite catalyst constitutes one kind of promising candidate for the nitrile gas SCC abatement. As reported by Kröcher and Elsener [4], similarly high HCN conversion activity (100% HCN conversion at 250–300 °C), but, much better N₂ selectivity, was found for the Cu-ZSM-5 with respect to those of Pd- and Pt-containing oxidation catalysts. Nanba et al. [5–7] reported that Cu-ZSM-5 also exhibited high catalytic activity and N₂ selectivity for AN-SCC, achieving AN conversion of 100% and N₂ selectivity > 95% at T > 350 °C [7]. The cationic Cu²⁺ exchanged at the Brønsted acid site acted was reported to be the active center and related redox ability (Cu²⁺ ↔ Cu¹⁺) played an important role in both AN conversation activity and N₂ selectivity [6]. In our previous works [9,10], a series of metal modified mesoporous M-SBA-15 (M = Cu, Co, Fe, V, Mn, Pd, Ag,

* Corresponding author.

E-mail address: zhangrd@mail.buct.edu.cn (R. Zhang).

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Pt) was prepared and further investigated for CH₃CN- and AN-SCC. Among them, the Cu modified mesoporous SBA-15 exhibited the best catalytic behavior, obtaining nearly a complete CH₃CN or AN conversion associated with a N₂ selectivity around 80% at T > 350 °C.

As for nitrile gas SCC mechanism, there have also been some of works reported based on zeolitic catalyst. Kröcher and Elsener [4] employing the in situ diffuse reflectance infrared Fourier transform spectra (in-situ DRIFTS) revealed that the HCN-SCC could follow an oxidation mechanism over Cu-ZSM-5. The HCN could be firstly oxidized into an intermediate of isocyanic acid (HNCO). The further oxidation of HNCO could produce the final products N₂, CO₂ and H₂O. Nanba et al. [7] utilizing in-situ DRIFTS investigated the AN-SCC mechanism over Cu-ZSM-5. It was suggested that the related mechanism mainly contained three parts: (i) C₂H₃-CN bond broke up to generate the intermediates of NCO, nitrate species, and C₂H₃ radical; (ii) part of NCO could be hydrolyzed into NH₃ which was then oxidized into N₂ and H₂O; part of NCO could react with the surface nitrate species to produce the final product of N₂; (iii) the C₂H₃ radical could be readily oxidized into CO₂ and H₂O. In our previous works [9,10], the CH₃CN- and AN-SCC mechanism over metal modified M(Cu, Co, Fe, V, Mn, Pd, Ag, Pt)/SBA-15 mesoporous catalysts were also investigated based on in-situ DRIFTS. Four kinds of reaction mechanisms were proposed: (a) N₂ formation mechanism for Cu/, Mn/and Ag/SBA-15; (b) NH₃ formation mechanism for Fe/, and V/SBA-15; (c) N₂O formation mechanism for Pt/, Pd/SBA-15 (at low temperature); (d) and NO formation mechanism for Co/SBA-15 and Pt/, Pd/SBA-15 (at high temperature).

Although parts of works have been reported for the nitrile gas SCC abatement, the related reaction system is still far from well established. Especially due to the limitation of the experimental approaches, the deeper mechanistic insight is still unknown. However, thanks to the quick development of computational chemistry, the quantitative chemistry based on density functional theory (DFT) provided an efficient method to shed more light on the complicated reaction mechanism, such as reaction routes, energy barriers, and structure parameters of generated intermediates. For example, Czekaj et al. [11] utilizing DFT gave a detailed hydrolysis reaction pathway of HNCO over the (101) surface plane. Barbosa and van Santen [12] employing DFT systematically investigated CH₃CN hydrolysis mechanism based on a 4T zeolitic cluster model. Three main reaction steps were proposed: hydration reaction, isomerization, and products desorption, among which the nucleophilic of H₂O in hydration reaction step was reported to be the rate-limiting step due to the highest reaction energy barrier.

In present work, the HCN-SCC over zeolitic catalysts was systematically investigated by employing both experimental and theoretical approaches: (i) firstly a series of Cu-(Beta, ZSM-5, FER, MCM-22, MCM-49, MOR) and M (M = Cu, Co, Fe, Mn, Ni)-ZSM-5 catalysts was prepared by impregnation method and characterized by BET, X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR); (ii) then the related catalytic behaviors, including HCN conversion, N₂ and CO₂ yield, were evaluated and compared with each other; (iii) finally the DFT was employed to give much deeper insight into HCN-SCC mechanism over the best performing zeolite catalyst, base on which the detailed reaction routes, energy barrier and microkinetic analysis were well illustrated.

2. Experimental and theoretical methods

2.1. Catalyst preparation

The parent zeolites (H-ZSM-5, H-FER, H-Beta, H-MOR, H-MCM-22, and H-MCM-49) utilized in present work were commercial products produced by Shanghai Novel Chemistry Company and with similar Si/Al ratio of 30. The parent zeolites were further modified by wetness impregnation method and with a total metal loading amount of 1 wt%. The detailed preparation strategies are as follows: (i) a certain amount of bare zeolite catalyst were impregnated into a deionized water

solution; (ii) a desired amount (50 mL of 2.5×10^{-2} M) of metallic nitrate [M(NO₃)_x] was thereafter added into the solution; (iii) after sufficient mixing for 24 h, the mixture was thereafter transferred into a vacuum evaporator to eliminate the solvent; (iv) the residue was dried at 110 °C for 2 h and further calcined at 550 °C for 4 h to obtain the final product.

2.2. Catalyst characterization

X-ray diffraction (XRD) experiments were conducted via X-ray diffractometer (Germany Bruker D8 type) with Cu K α irradiation and nickel filter ($\lambda = 1.5406 \text{ \AA}$). It was operated at 40 kV and 200 mA. The crystal phases were thereafter verified according to the JCPDS card. The metal loading amount of the prepared samples was determined by AXIOS advanced wavelength dispersive X-ray fluorescence spectrometer (XRF) (PANalytical).

The specific surface area (S_{BET}) and Micropore volume (V_{micro}) was measured through nitrogen adsorption/desorption at 77 K using a Sorptomatic 1990 instrument (Thermo Electron). S_{BET} was obtained according to Brunauer-Emmett-Teller (BET) method and V_{micro} was determined by t-plot method.

H₂-temperature programmed reduction (H₂-TPR) were performed on a Thermo Electron TPD/R/O 1100 Series instrument equipped with a thermal conductivity detector (TCD) which could on-line monitor H₂ consumption. The samples (about 0.1 g) were pretreated by 20 mL min⁻¹ N₂ flow at 100 °C for 30 min, then exposed to 20 mL min⁻¹ of reducing gas (5% H₂ balanced by N₂) and heated at a ramp of 5 °C min⁻¹ from 100 to 750 °C. In order to make quantitative calculation of H₂ consumption, the TCD signal was further calibrated based on standard sample of CuO. Thereby, the H₂ consumption of each sample could be derived by integration of H₂-TPR peak areas.

2.3. Activity measurement

Activity tests for HCN oxidation were carried out through a fixed-bed reactor under atmospheric pressure in the temperature range of 200–550 °C. The reactant gas mixtures, consisting of 1200 ppm HCN, 3 vol% O₂ balanced by He (> 99.999%), were fed into the reactor in a total flow of 80 mL min⁻¹ (GHSV = 20,000 h⁻¹). The concentration of the effluent gases (HCN, CO, CO₂, NH₃, N₂O, NO and NO₂) were monitored via an infrared gas analyzer (Nicolet Nexus 470), while N₂ and O₂ were recorded by a gas chromatograph (GC, HP5890) fitted with a TCD. As noted, the whole reaction system was conducted in a fume hood.

2.4. Computational method and constructed models

The DFT simulations of present work were implemented in Gaussian 09 suite of programs [13]. The algorithm of DFT was combined with the Becke three-parameter hybrid method, by using the LYP correlation function (B3LYP) [14]. The core electrons of the Cu atom were represented by the LANL2DZ effective core potential (ECP), and its valence electrons were described by the LANL2DZ basis set. For atoms of Si, Al, O, N and H, the common basis set 6-31G(d) was used during the calculations of geometry optimization (GO), transition state (TS) and intrinsic reaction coordinate (IRC), while the high level basis set 6-311++G(d,p) was used for energy calculation. During the geometry optimization, all the models were confirmed as the stationary point by frequency calculations. The TS clusters were identified by both the frequency calculations and the IRC analyses.

According to the literature report [15], the most stable site for Al substitution was T12 site in ZSM-5. Therefore, the 20T Cu-ZSM-5 models, containing a double 10 membered ring (bi-layer of main channel of MFI) and with the atomic Al being located at the T12 site, were constructed in present work. The skeleton of ZSM-5 with MFI structure topology was subtracted from Material Studio 4.0 package.

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