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Full Length Article

Coupling catalytic hydrolysis and oxidation on Mn/TiO_2-Al_2O_3 for HCN removal

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ABSTRACT

The manganese-modified titania-alumina (Mn/TiO_2-Al_2O_3) catalyst synthesized by sol–gol method was used to remove hydrogen cyanide (HCN) from simulated flue gas. Further, effects of the mass ratios of Ti/Al, Mn loading, calcination temperature, and relative humidity on HCN conversion efficiency and catalytic activity were systematically investigated. The results indicated that the Mn/TiO_2-Al_2O_3 catalyst exhibited significantly enhanced HCN removal efficiency, and the maximum yield of N_2 increased to 68.02% without the participation of water vapor. When water vapor was added into the flue gas, the yield of N_2 decreased and the formation of NO_x was also inhibited. The XRD and XPS results indicated that Mn was mainly present in the form of Mn^{2+}, Mn^{3+}, and Mn^{4+} on the surface of catalyst and chemisorbed oxygen played a major role in the HCN catalytic oxidation process. The results of DSC-TGA analysis and H_2-TPR indicated that the catalyst also exhibited a good thermal and chemical stability. NH_3-TPD and CO_2-TPD indicated that the surface of the catalyst mainly contained acidic sites. During the reaction, part of NH_3 was adsorbed by Brönsted and Lewis acid sites. NH_3 adsorbed on Lewis acid sites participated in NH_3-SCR, which reduced the amount of NO_x produced and resulted in a high N_2 yield.

1. Introduction

Hydrogen cyanide (HCN) as a volatile strong toxic gas, not only poses serious hazards to the human health, but also causes significant environmental damage. It is also one of the most "special" wastes and harmful pollutants present in industrial waste gas [1]. HCN is usually derived from the exhaust of motor vehicles [2], selective catalytic reduction (SCR) of nitrogen oxides (NO_x) and hydrocarbons [3–5], the well-established three-way-catalyst process [6], urea-SCR processes [2], biological and fossil fuel combustion, and oil processing processes [7–9]. Yellow phosphorus tail gas is also one of the sources of HCN. The main component of the exhaust gas is carbon monoxide (CO), which is an important and attractive chemical raw material in C1 building block chemical industry [10,11]. However, the yellow phosphorus tail gas contains variety of harmful gaseous species coexisting with CO, low oxygen content, and encounters comprehensive purification difficulties; therefore, its effective utilization is extremely difficult. In order to make complete use of CO to synthesize various compounds with economic value, purification of yellow phosphorus tail gas is highly desirable. The impurity gas HCN in the yellow phosphorus tail gas leads to the poor activity or poisoning of the carbonyl synthesis catalyst and shift catalyst. Furthermore, the presence of HCN also significantly reduces the removal efficiency of sulfides and produces slow and long-term corrosion of industrial pipelines [12]. Moreover, HCN is considered to be the main intermediate for NO_x, such as N_2O, NO_2, NO, which can lead to greenhouse effect and generation of photochemical fumes [13,14]. Therefore, the removal of HCN from the yellow phosphorus tail gas is an important research hot topic. In order to avoid HCN emissions from exhaust, catalytic oxidation (1) or hydrolysis (2) of HCN are considered to be the effective solutions [15] as follows:

$$4HCN + 5O_2 = 4CO_2 + 2N_2 + 2H_2O \quad (1)$$

$$HCN + H_2O = NH_3 + CO \quad (2)$$

Zhao et al. [16] conducted detailed catalytic oxidation of HCN using a 0.5% Pt/Al_2O_3 catalyst. The main reaction products were N_2, N_2O, NO, NO_2, CO_2, and H_2O; however, the other reduced species such as ammonia (NH_3) and CO were not formed due to strong oxidizing conditions employed in their study. Furthermore, they also reported that in the reaction of HCN with O_2 at 250 °C, the maximum selectivity for N_2 was ca. 25%. However, when the system simultaneously introduced water vapor, no effect on HCN conversion or N_2 selectivity was observed. O. Kröcher and coworkers [17] tested titania (TiO_2) hydrolysis catalyst, which enabled quantitative conversion of HCN to CO and NH_3. Alumina (Al_2O_3)

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has also been used as a hydrolysis catalyst; however, the removal rate of HCN was about 50% lower. MnO_x/Al_2O_3 and MnO_x/TiO_2 have also been used for the SCR of NO_x by NH_3 at low-temperature, selective catalytic oxidation (SCO) of NH_3 to N_2, and catalytic oxidation of NO. It has also been reported that MnO_x exhibit the desirable performance attributed to their high catalytic activity [18–20]. Mn^{4+} species were found to be the most active components among the various Mn valence states. Conversion of Mn^{4+} to Mn^{3+} plays an important role in this reduction reaction [21–23]. Numerous studies have reported the advantage of excellent features of Al_2O_3-modified TiO_2 over either pure TiO_2 or pure Al_2O_3 [24–26]. According to literature, TiO_2 showed excellent hydrolysis property toward HCN, which could occur even in the absence of water [6]. However, its thermal stability and oxidation property were found to be very poor, which significantly affected the activity of catalyst. Therefore, TiO_2-Al_2O_3 has attracted significant attraction as a composite because of its excellent corrosion resistance effects, large specific surface area (SSA), special redox properties, and catalytic behavior [27–29]. Furthermore, the metal skeleton structure of the composite carrier TiO_2-Al_2O_3 can also be improved by adding a small amount of Al metal, which results in improvement of the thermal stability of the catalyst.

Based on above mentioned considerations, in this study, Mn-modified TiO_2-Al_2O_3 (Mn/TiO_2-Al_2O_3) catalyst was fabricated by sol–gel method, and it was utilized for the effective removal of HCN by the synergistic effect of catalytic hydrolysis and catalytic oxidation. Further, the effects of Ti and Al mass ratio, content of metal Mn, calcination temperature, and relative humidity on HCN removal efficiency and N_2 product yield were systematically investigated to obtain the catalyst with optimal performance. The surface structure and chemical properties of the catalysts were characterized by Brunauer–Emmett–Teller (BET) method, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Hydrogen-temperature programmed reduction (H_2-TPR), differential scanning calorimetry-thermogravimetric analysis (DSC-TGA), NH_3-temperature programmed desorption (NH_3-TPD), and CO_2-TPD.

2. Experimental

2.1. Fabrication of catalyst

The Mn/TiO_2-Al_2O_3 catalyst was fabricated by sol–gel method. Manganese(II) acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$, 99.9%, Aldrich), butyl titanate ($Ti(OC_2H_5)_4$, 97%, Aldrich), and aluminum isopropoxide ($Al(O\text{-}i\text{-}Pr)_3$, 99%, Aldrich) acted as the precursors of active component and supports, respectively. First, a certain amount of $Ti(OC_2H_5)_4$ was added to anhydrous ethanol, then the corresponding proportions of citric acid (citric acid/Mn = 1, molar ratio) were added, and the solution was stirred gently at 60 °C for 20 min. Second, acetic acid and $Al(O\text{-}i\text{-}Pr)_3$ were successively added to the mixture, and the resulting solution was allowed to stir vigorously with a magnetic stirrer for 1 h at 40 °C. $Ti(OC_2H_5)_4$, deionized water, anhydrous ethanol, and glacial acetic acid were present in the volume ratio of 1:1:5:0.5. The freshly prepared $Mn(CH_3COO)_2{\cdot}4H_2O$ solution was dropped slowly into the mixture. The final mixture was stirred continuously at temperature below 60 °C until it changed to a viscous gel. Then it was dried at 80–120 °C for 5–8 days until the dry-gel was obtained. Finally, dry-gel was calcined at 550 °C for 5 h in muffle furnace. The total metal mass percentage was calculated by using the equation (Mn/(Mn + Ti + Al)) for each catalyst.

2.2. Activity measurements

Experimental apparatus is mainly composed of the following three parts: mixed gas preparation chamber, reactor (heating rate: 10 °C min^{-1}), and exhaust gas analysis section. The reaction was performed in a quartz U-tube reactor with 8 mm inner diameter and 150 mm length at temperature in the range of 100–350 °C. The dosage of catalyst was 0.2 g. The simulated gas stream consisted of 100 ppm HCN, 0.2–1% O_2, 0–20% relative humidity, and N_2 (experimental gas was obtained from Kunming Messer Gas Products Co., Ltd., China) as the balance gas. The gas hourly space velocity (GHSV) was controlled at 32,000 h^{-1}.

N_2O was monitored by gas chromatography (FULI GC-9790II, China) and NO_x (NO, NO_2) were measured by flue gas analyzer (ecom-EN2, Germany). HCN and NH_3 were analyzed using a mass spectrometer (MAX300-LG) and an NH_3 detecting pipe, respectively. Concentration of N_2 was determined from the N-balance based on the N-containing reaction products [17] as represented by Eq. (3):

$$C_{N_2} = \frac{C_{N-in} - C_{NH_3-out} - C_{NO_x-out} - C_{HCN-out}}{2} - C_{N_2O-out} \quad (3)$$

In this study, it was assumed that all missing N was converted to N_2, and the C_2N_2 was too little that could be ignored based on the N-balance. The conversion rate and products yields of HCN are calculated as follows [26]:

$$Y_{HCN-conversion} = \frac{C_{HCN-in} - C_{HCN-out}}{C_{HCN-in}} \times 100\% \quad (4)$$

$$Y_{NH_3} = \frac{C_{NH_3-out}}{C_{HCN-in} - C_{HCN-out}} \times 100\% \quad (5)$$

$$Y_{N_2} = 2\frac{C_{N_2-out}}{C_{HCN-in} - C_{HCN-out}} \times 100\% \quad (6)$$

$$Y_{NO_X} = \frac{C_{NO_X-out}}{C_{HCN-in} - C_{HCN-out}} \times 100\% \quad (7)$$

$$Y_{N_2O} = 2\frac{C_{N_2O-out}}{C_{HCN-in} - C_{HCN-out}} \times 100\% \quad (8)$$

2.3. Characterization of catalyst

Surface area, pore size distribution, and pore volume were measured through nitrogen adsorption–desorption isotherms at 77.35 K using a multi-spot nitrogen analyzer (NOVA2000e, Quantachrome Corp.). XRD patterns of the catalysts were observed using a Brucker D8 Advance system with Cu Kα radiation at 45 kV and 200 mA. The surface state of the catalyst sample was analyzed by XPS (Thermo ESCALAB 250XI, USA). Thermal stability of the catalyst was examined through the instrument: SDT Q600 V20.9 Build 20, USA. The Mn/TiO_2-Al_2O_3 catalyst was exposed to a flow of NH_3 or CO_2 for 1 h. Then the catalyst was heated in helium from 50 to 800 °C at a rate of 10 °C min^{-1} to desorb NH_3 (NH_3-TPD) or CO_2 (CO_2-TPD). During H_2-TPR, a feed of 5 vol% of H_2 in N_2 was used to reduce the catalyst with continuous temperature ramp at a flow rate of 30 mL min^{-1}, and then catalysts were treated by increasing temperature from 50 to 800 °C at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Effect of carrier and active component on HCN conversion rate

Fig. 1 shows the effect of different Ti and Al mass ratios on the conversion of HCN. Clearly, the effect of TiO_2-Al_2O_3 on the conversion of HCN becomes better with the increase in the mass ratio of Ti to Al. When Ti:Al = 8:2, TiO_2-Al_2O_3 exhibits the best conversion rate toward HCN. This result is attributed to the fact that TiO_2 has a good low temperature hydrolysis effect, thus it leads to the