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Removal of Gas Phase Low-concentration Toluene by Intermittent Use of Adsorption and Non-thermal Plasma Regeneration

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Abstract: Removal of gas phase low-concentration toluene is investigated by intermittent use of adsorption and non-thermal plasma regeneration over catalysts including Ag/HZSM-5, Mn/HZSM-5, Ce/HZSM-5, Ag-Mn/HZSM-5 and Ce-Mn/HZSM-5. Results show that Ag-Mn/HZSM-5 displays the best catalytic performance as well as excellent toluene adsorption capability, making it a promising catalytic material for toluene removal in indoor air.

Keywords: VOCs, Adsorption, Non-thermal Plasma.

1. Introduction

Low-concentration volatile organic compounds (VOCs) remain the major pollutants in Chinese households and have sparked growing public concern in recent years due to their adverse health effects [1-2]. Plenty of studies have been made for removing VOCs from gas streams. However, since concentrations of VOCs in indoor air are much lower and treatment of indoor air has to be conducted at room temperature with limited secondary pollutants, traditional air pollution control technologies are not fit for indoor air treatment.

As an alternative approach, non-thermal plasma (NTP) technology may be more appropriate for indoor air purification because it is capable of removing various indoor pollutants such as particulate matters, bacteria and VOCs simultaneously under ambient conditions [3]. Nevertheless, there are still some drawbacks such as low energy efficiency, poor selectivity towards total oxidation and undesired byproduct formation [4–6] in removing low-concentration VOCs in indoor air. To solve these problems, much effort to combine plasma technology with heterogeneous catalysis has been undertaken for more than three decades [7-10].

Ogata et al. have found the decomposition efficiency of benzene in the zeolite-hybrid reactor was 1.4-2.1 times higher than in a conventional plasma reactor and pointed out that the decomposition energy efficiency could likely be improved if the adsorption and plasma discharge were carried out cyclically at optimized intervals [11]. Based on this finding, intermittent use of adsorption and plasma regeneration has been explored recently [12-17] to further reduce energy consumption. Briefly, this technique is operated in two steps: the low-concentration VOCs in air are first adsorbed on catalysts with plasma off and then the adsorbed VOCs are oxidized by turning plasma on. Kuroki et al. have demonstrated the repeatability of adsorption and plasma regeneration by using hydrophobic zeolite honeycomb as the adsorbent and found it an extremely effective and practical VOCs removal process [12, 13]. It has also been reported that high oxidation rate of absorbed benzene as well as low energy cost could be achieved when an intermittent adsorption and plasma regeneration was used to remove benzene [15] and formaldehyde [16, 17] with oxygen plasma. However, oxygen plasma is extremely difficult to realize due to the characteristics of indoor air treatment and the problem of ozone production cannot be avoided with oxygen plasma, which is not investigated in detail in these studies.

At present, intermittent adsorption and plasma regeneration are applied to remove low concentration of toluene in indoor air. This work is mainly designed to further demonstrate the feasibility of this method when operated in air. Byproducts formation as well as the toluene conversion and CO_x evolution are systemically investigated. Besides, different catalysts including Ag/HZSM-5, Mn/HZSM-5, Ce/HZSM-5, Ag-Mn/HZSM-5, Ce-Mn/HZSM-5 are compared both by their adsorption capacity and catalytic performance.

2. Experimental

2.1. Experimental setup

Fig.1 presents the schematic diagram of the experimental system. It consists of a tandem plasma-adsorption/catalyst system, gas supply and analytical instrumentation. The plasma-adsorption/catalyst system contains two reactors: the first is a link tooth wheel-cylinder DC plasma reactor; the second reactor with an inner diameter of 10 mm is an adsorption/catalyst reactor. Catalyst is introduced in the second reactor and supported by a glass sieve plate.

2.2. Experimental methods

For preparation of the Ag/HZSM-5, Mn/HZSM-5, Ce/HZSM-5, Ag-Mn/HZSM-5 and Ce-Mn/HZSM-5 catalysts, HZSM-5 powder is impregnated in the corresponding metal nitrates aqueous solution of desired concentration, followed by evaporation to dryness in a rotary evaporator at 343 K. The resulting samples are then dried at 378 K for 12 h and calcined in air at 773 K for 5 h to obtain the desired catalysts.

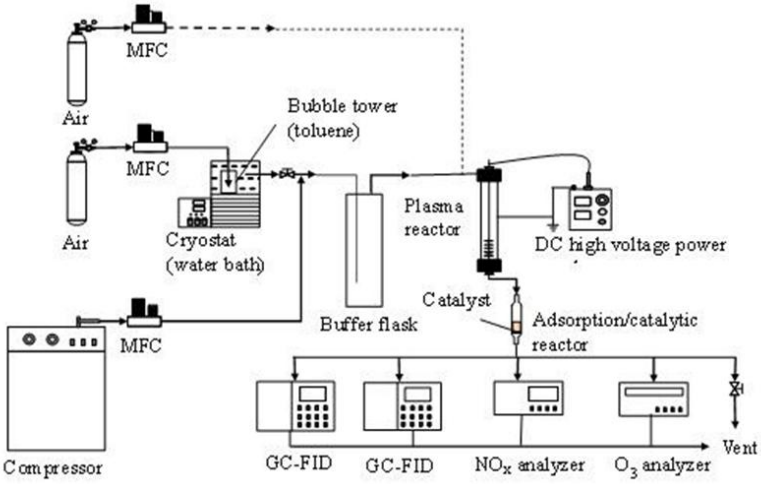

Fig. 1 Schematic diagram of the experimental setup

Gaseous toluene is introduced by passing compressed air through a temperature-controlled bubble towers containing liquid toluene, and is completely mixed with the dilution air in a buffer flask before the plasma reactor for the adsorption process. The flow rates of air are adjusted by a set of mass flow controllers. The gas containing 3-ppm toluene passes through the adsorption/catalyst reactor for adsorption at a rate of 3.0 L/min, with the residence time in the catalyst being 0.046 s. Toluene concentration is analyzed by using an on-line gas chromatography (Agilent, model 6890N), equipped with a flame ionization detector (FID) and a 30-m HP-5 capillary column. For the plasma regeneration process, synthetic air with the flow rate of 1.0 L/min is used. The temperature of gas is 298 ± 1 K while its relative humidity is 40 ± 5%.

Generally, the complete oxidation of toluene to CO_2 and H_2O cannot be achieved. As a result of incomplete oxidation, CO and other intermediates are often observed. In this study, the outlet concentrations of CO and CO_2 are detected by its conversion to CH_4 in a homemade methanator at 653K and corresponding concentration of CH_4 is measured by an on-line gas chromatography (Techcomp, model GC7890II) with an FID.

As long as the plasma regeneration process is operated in air-like mixtures, the formation of O_3 and nitrogen oxides will be unavoidable, which are also serious air pollutants. The O_3 concentration at the plasma regeneration stage is monitored by an ozone analyzer (2B Technologies, 106-M). A Thermo Scientific model42i Chemiluminescent NO–NO_2–NO_x analyzer (USA) is used for monitoring nitrogen oxides production.

The examined parameters, toluene conversion to CO_x ($S_{C_7H_8\to CO_x}$, %), CO_2 selectivity (S_{CO_2} , %), CO selectivity (S_{CO} , %) and energy consumption are defined as follows:

$$C_{C_7H_8\to CO_x}(\%)=\frac{n_{CO_2}+n_{CO}}{7\times C_{C_7H_8}+n_{CO}}\times 100\%, \quad (1)$$

$$S_{CO_2}(\%)=\frac{n_{CO_2}}{n_{CO_2}+n_{CO}}\times 100\%, \quad (2)$$

$$S_{CO}(\%)=\frac{n_{CO}}{n_{CO_2}+n_{CO}}\times 100\%, \quad (3)$$

$$E_C(\mathrm{kWhm^3})=\frac{UIt_2}{60\times(Q_1t_1+Q_2t_2)}, \quad (4)$$

where $n_{C_7H_8}=\int_0^{t_1} c_{C_7H_8}Q_1t_1$, $n_{CO_2}=\int_0^{t_2} c_{CO_2}Q_2t_2$, $n_{CO}=\int_0^{t_2} c_{CO}Q_2t_2$; $C_{C_7H_8}$ is the difference between outlet and inlet toluene concentrations of an adsorption stage, and are the concentrations of CO and CO_2 in the gas stream of a plasma regeneration stage; Q_1 and t_1 are the total flow rate (Lmin-1) and the adsorption period (min) at the adsorption stage respectively; Q_2 and t_2 are the total flow rate (Lmin-1) and the plasma regeneration period (min) at the plasma regeneration stage respectively; U and I are the discharge voltage (kV) and current at the plasma discharge stage respectively.

3. Results and discussion

3.1 Adsorption capacity of different catalysts

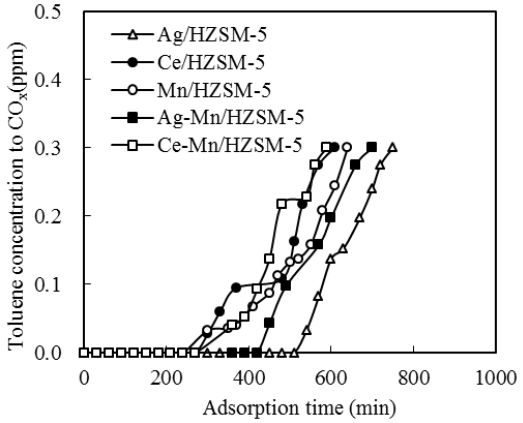

Fig. 2 Comparison of breakthrough curves on different catalysts for toluene

Breakthrough curves for toluene adsorbed on different catalysts are shown in Fig. 2. Initially, the injected toluene is completely adsorbed on each catalyst. As toluene coverage on catalyst surfaces increases, the sticking probability of toluene decreases. Consequently, the toluene outlet

concentration increases. However, the difference in breakthrough times (time for reaching Cout/Cin= 0.1, Cout and Cin are outlet and inlet concentrations, respectively) are found among different catalysts. It is apparent that catalysts loaded with Ag (Ag/HZSM-5 and Ag-Mn/HZSM-5) have longer breakthrough time (more than 10h) than other catalysts. These results may owe to the Ag which can form the normal σ bond to carbon as well as bonds with unsaturated hydrocarbons in a nonclassical manner according to the unique characteristics of the orbitals in this metal or ions [18]. On the other hand, the adsorption capacity of Ag/HZSM-5 decreases to a certain degree after the addition of Mn due to the declining of the BET surface area. According to previous studies, better adsorption capacity can help reduce the overall energy consumption of the process [17]. Therefore, the long breakthrough time for low-concentration toluene make Ag/HZSM-5 and Ag-Mn/HZSM-5 suitable for the intermittent use of adsorption and plasma regeneration.

In addition, Y zeolites, CeO_2 and Al_2O_3 are also tested as catalyst carriers. However, their performance in absorbing toluene is much poorer when compared to HZSM-5 and hence are not further investigated.

3.2. Toluene conversion

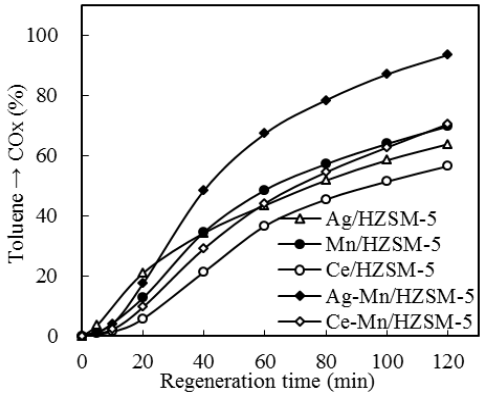

Fig. 3 Comparison of toluene concentration to CO_x as a function of regeneration time

To investigate the catalytic performance of different catalysts, plasma regeneration is performed after 8 hours of absorption. The toluene conversion, CO_x selectivity and byproducts production are compared among different catalysts.

Fig. 3 exhibits the conversion profiles of toluene to CO_x as functions of regeneration time. As for different catalysts, the conversion is in the order of Ag-Mn/HZSM-5>Mn/HZSM-5>Ag/HZSM-5> Ce-Mn/HZSM-5>Ce/HZSM-5, which demonstrates that Mn/HZSM-5 performs better in toluene catalytic oxidation than Ag/HZSM-5 and Ce/HZSM-5. And the addition of Ag to Mn/HZSM-5 can improve the conversion from 69% up to more than 93%. It is well known that the oxidation of organic molecules over manganese oxide catalysts may involve a Mars-van Krevelen type mechanism, where the organic molecule is oxidized by lattice oxygen of metal oxides, the latter being reoxidized by gas phase oxygen [19]. Thus, the oxidation of toluene may be significantly affected by lattice oxygen of manganese oxides. Qu et al. have reported that the ratios of lattice oxygen to surface-absorbed oxygen on the Mn catalysts is enhanced with appropriate Ag addition [20], which may explain the high toluene conversion on Ag-Mn/HZSM-5.

Synthetic air without toluene is used for plasma regeneration, so desorption of toluene driven by the concentration grads may occur. Toluene desorption is found for Mn/HZSM-5, Ce/HZSM-5 and Ce-Mn/HZSM-5 catalysts. On the contrast, no toluene is detected in the outlet air for Ag/HZSM-5 and Ag-Mn/HZSM-5 catalysts. These results may be explained by the strong toluene adsorption of Ag.

Mn/HZSM-5, Ce/HZSM-5, Ag-Mn/HZSM-5 and Ce-Mn/HZSM-5 during the regeneration process.

Herein, the energy consumption is calculated to be 2.2×10-3 kWhm-3. This extremely low energy cost in removing low-concentration toluene from air provides significant proof for the practical application of this method in indoor air purification. In fact, as toluene concentration in actual environment is much lower than 3-ppm, the adsorption time can be much longer, resulting in lower energy consumption.

3.3. CO_x evolution

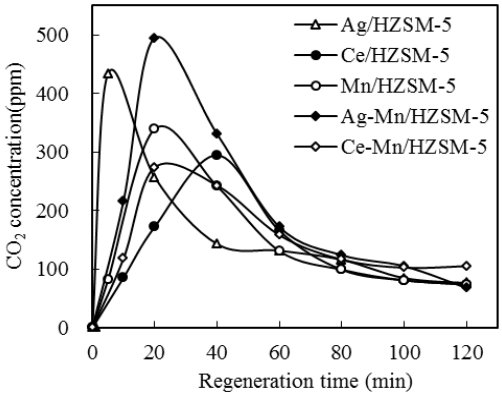

Fig. 4 Comparison of CO_2 evolution during the regeneration process

Since the adsorbed toluene is mostly oxidized to CO_x, the CO_x evolution on different catalysts is investigated. As seen from Figs. 5 and 6, CO_2 and CO outlet concentrations firstly increase to the maximum and then decrease slowly, indicating that the adsorbed toluene is oxidized rapidly with the plasma on and the reaction rate decreases as the regeneration progress proceeds. It also illustrates that the concentration of CO_2 peaks at different times for different catalysts. Ag/HZSM-5 has the shortest time, while Ce/HZSM-5 the longest. Consistent with the results of toluene conversion, the maximum concentration of CO_2 for Ag-Mn/HZSM-5 is much higher than for other investigated catalysts, which further proves that toluene oxidation is more complete on theAg-Mn/HZSM-5 catalyst. On all of the investigated catalysts, more than 90%

CO_2 selectivity is achieved. Moreover, on Ag-Mn/HZSM-5 catalyst CO_2 is produced with 99.9% selectivity.

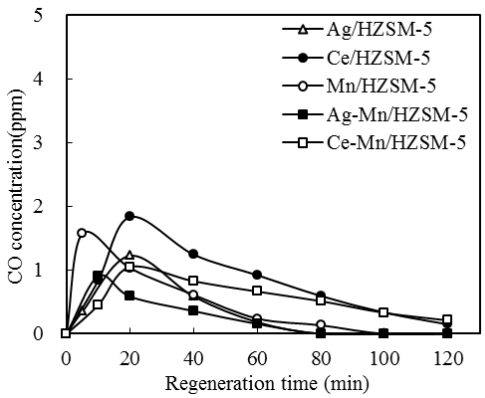

Fig. 3 Comparison of CO evolution during the regeneration process

3.4. Byproducts formation

Consistent with the toluene conversion results, Mn/HZSM-5 is found out to be more effective in catalytically decomposing O_3 than Ag/HZSM-5 and Ce/HZSM-5. And Ag-Mn/HZSM-5 results in the least O_3 emission compared with the other investigated catalysts. Since the decomposition of O_3 on the catalysts can produce active oxygen species, the high toluene conversion of Ag-Mn/HZSM can be explained by its good O_3 decomposition property.

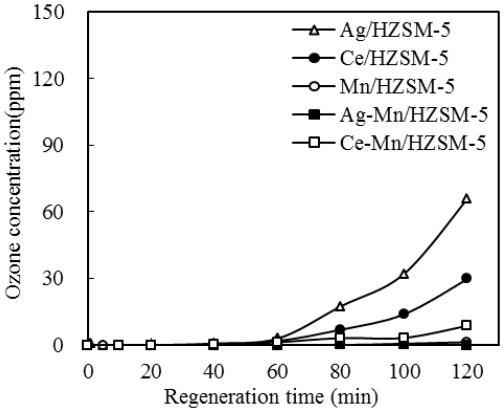

Fig. 4 Comparison of O_3 evolution during the regeneration process

For NO_x, only NO_2 is detected in the outlet gas. Results have shown that the NO_2 outlet concentration is less than 50 ppb with all of the investigated catalysts.

4. Conclusion

Intermittent use of adsorption and plasma regeneration for gas phase low-concentration toluene removal is systematically studied in this paper when Ag/HZSM-5, Mn/HZSM-5, Ce/HZSM-5, Ag-Mn/HZSM-5 and Ce-Mn/HZSM-5 are used as catalysts. The main findings are as follows:

(1) Catalysts loaded with Ag (Ag/HZSM-5, Ag-Mn/HZSM-5) have larger adsorption capacity for toluene than the other investigated catalysts.

(2) Ag-Mn/HZSM-5 shows the best toluene oxidation property in both promoting the toluene conversion and reducing the emission of O_3.

(3) Intermittent use of adsorption and plasma regeneration can reduce energy consumption with limited byproducts, providing significant proof for practical application of this method in indoor air purification.

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